

APPENDIX C

SUMMARY OF PRELIMINARY INVENTORY

TABLE OF CONTENTS

	<u>Page</u>
C-1.0 PRELIMINARY INVENTORY BY DEVICE TYPE	C-1
C-2.0 PRELIMINARY INVENTORY BY APPLICATION	C-4
C-3.0 PRELIMINARY INVENTORY UNCERTAINTY	C-9
REFERENCES	C-11

Blank Page

APPENDIX C

SUMMARY OF PRELIMINARY INVENTORY

A preliminary inventory of SOx emissions in the South Coast Air Basin was prepared for the purpose of identifying the major sources, estimating emissions and establishing priorities for a test program to resolve uncertainties that are apparent in the preliminary data. Portions of the preliminary inventory results are reproduced in this appendix to provide the background on which the field test program and further data gathering were based.

The preliminary inventory was based largely on the recent inventory of NOx (Ref. 1) conducted by the ARB. The inventory period for that program was the fiscal year of July 1972 through June 1973. Information on device operating capacity and fuel use gathered for that survey was retained for the preliminary inventory. However as discussed in Section 3 the final results of the current program are based on the calendar year 1974 and updating of the most significant sources to this period was performed for the final inventory..

C-1.0 PRELIMINARY INVENTORY BY DEVICE TYPE

The preliminary inventory of stationary SOx points sources sorted by device type is given in Table C-I for the total Basin. The most significant result is the difference in the summer and winter total SOx emissions of 159 and 515 tons as SO₂/day respectively. The difference is attributable primarily to the fuel burning sources; boilers for which gas is the main summer fuel and oil the main winter fuel. For other devices where processed material is the primary source of SOx and summer and winter differences are less apparent.

In the summer months furnaces and kilns contribute 41% of the SOx, with coke kilns and primary metal furnaces predominating. Petroleum fluid catalytic cracking, contributing 36%, and sulfur recovery plants, emitting 13%, are also large sources of emissions in the summer.

TABLE C-I

SOx PRELIMINARY INVENTORY BY DEVICE TYPE

Device	Number	Daily SOx Emissions, Tons SOx as SO ₂ /Day		
		August	December	Annual
I. BOILERS	680	2.27	329.58	184.50
A. Utility	70	0.56	313.40	179.89
B. Industrial-Refinery	78	0.96	4.53	3.63
C. Industrial-Other	288	0.74	9.06	0.88
D. Coml/Inst.	244	0.00	2.59	0.10
II. FURNACES, KILNS		65.17	75.99	64.38
A. Coke/Carbon	6	29.22	29.55	28.00
B. Primary Metals	63	22.12	27.49	21.80
C. Aggregate	7	6.41	6.42	6.41
D. Secondary Metals	73	4.87	5.63	4.95
E. Cement	10	0.00	3.76	1.00
F. Glass	26	2.51	2.72	2.18
G. Other	80	0.04	0.42	0.04
III. PETROLEUM CRACKING				
A. Fluid Catalytic	8	57.10	63.85	59.89
IV. SULFUR RECOVERY				
A. Claus Units	19	21.21	21.21	19.98
V. PROCESS HEATERS				
A. Petroleum	335	4.29	14.26	9.92
VI. OIL FIELD RECOVERY				
A. Vapor Phase Reactors	9	6.57	6.57	6.58
VII. SULFURIC ACID				
A. Contact Units	5	2.48	2.48	2.34
VIII. INTERNAL COMB. ENGINES		0.07	0.17	0.07
A. Gas Turbine	46	0.06	0.16	0.07
B. Reciprocating	98*	0.01	0.01	0.00
IX. MISCELLANEOUS	115	0.14	0.45	0.22
TOTAL	1580	159.30	514.56	347.88

*Groups of engines, total of 488 engines.

5802-432

In the winter 61% of the SOx is emitted by utility boilers. Winter emissions from furnaces and kilns, nearly the same as in the summer on an absolute basis, are only 15% of the total winter emissions. Petroleum fluid catalytic cracking units emit 12% of the winter SOx emissions. The remaining device groups are individually less than 5% of the winter emissions and together total 12%.

For emissions expressed on an annual basis, utility boilers are again the dominant source (52%). Furnaces and kilns contribute 19% and petroleum catalytic cracking 17%. The sulfur recovery units emit 6% and the remaining device groups individually are less than 4% and together total 11% of the annual emissions.

The emissions from 19 operating refinery sulfur recovery units should be viewed in the context of substantial reductions achieved by installation of tail gas clean-up units that have been installed on all plants. An estimate of SOx emissions that probably were emitted prior to these installations indicates a rate of about 112 tons as SO₂/day compared with the preliminary inventory value of about 20 tons/day. Of the latter amount 7 tons/day are emitted by 15 plants with properly operating tail gas units. The remaining 13 tons/day is emitted from 4 plants operating with tail gas units installed but not yet fully operational. When these units are properly operating the 20 tons/day will be reduced to an estimated 8 tons/day.

As previously noted the preliminary inventory is based on 1972/1973 data. Updating to a 1974 base period is expected to show an increase in summer emissions for utility boilers and possibly process heaters as natural gas was in shorter supply.

Detailed device breakdown by county will be provided for the final inventory. Emissions presented in this section are for total SOx. The distribution of SOx between SO₂ and SO₃ will also be provided on a device basis in the final inventory.

C-2.0 PRELIMINARY INVENTORY BY APPLICATION

The preliminary inventory of Basin SOx emissions sorted by application categories is summarized in Table C-II. Designation of emissions by application is the primary inventory procedure used by the various air pollution control districts.

Utilities produce the largest winter SOx emissions (61%) as the result of the curtailment of natural gas in the winter months when heating requirements are high. Summer emissions shown are less than 1 ton/day based on the assumption that for a typical day all power plants burn gas fuel. Actual emissions reported to the Air Pollution Control Districts (Ref. 21) averaged 22 tons/day in July 1972 and 41 tons/day in August 1972 although only 13% of the fuel energy used was from fuel oil. This difference between the inventory assumptions and actual reported emissions will be taken into account for the final inventory based on 1974 as oil use in the summer increased to about 50%. On an annual basis the utilities emit an average of 180 tons/day or 52% of the Basin SOx emissions.

Petroleum refineries emit 57% of the summer emissions and 22% of the winter emissions. The summer, winter and annual tonnage rates are nearly equal as refinery gas is the predominant fuel. Winter emissions are slightly higher than for summer as about 16% of the winter energy is provided by fuel oil. On an annual basis the refineries emit 100 tons of SOx per day or 29% of the Basin emissions.

The metals industry emits 17% of the summer emissions and 7% in the winter. Winter emissions are 35% higher compared with summer emissions as the result of increased oil use. On an annual basis 27 tons/day are emitted or 8% of the Basin emissions.

Emissions from the chemical industry are primarily from coke-to-carbon processing. Summer, winter and annual rates are nearly equal except for plastics where the use of oil fuel increases winter emission. Chemical plants emit 30 tons/day on an annual basis or 9% of the Basin emissions.

TABLE C-II

SOx PRELIMINARY INVENTORY BY APPLICATION CATEGORY

Application	Daily SOx Emissions, Tons SO ₂ /Day		
	August	December	Annual
UTILITY	0.56	313.48	179.93
PETROLEUM	90.38	111.08	100.33
INDUSTRIAL-METALS			
Iron & Steel	18.54	28.20	18.73
Lead and other	9.15	9.19	8.64
Aluminum	0.00	0.17	0.00
INDUSTRIAL-CHEMICAL			
Coke/Carbon	29.22	29.56	28.01
Sulfuric Acid	2.24	2.24	2.11
Plastics	0.06	1.76	0.17
Other	0.00	0.12	0.00
INDUSTRIAL-MINERALS			
Aggregate	6.41	6.41	6.41
Cement	0.00	3.79	1.01
Glass	2.51	2.79	2.18
Other	0.04	0.96	0.05
INSTITUTIONAL	0.01	1.89	0.09
INDUSTRIAL-UNCLASSIFIED	0.12	1.22	0.16
INDUSTRIAL-AGRI & FOOD	0.00	0.80	0.02
INDUSTRIAL-MFG, ASSEMBLY	0.06	0.46	0.03
COMMERCIAL	0.00	0.27	0.01
TOTALS	159.30	514.56	347.88

5802-432

In the mineral industry SOx emissions occur primarily from manufacture of construction aggregate and glass. Winter emission of 3.8 tons/day is indicated for cement plants for oil fuel burning. However, this must be reviewed for the final inventory as cement particulates may absorb most SOx. Annual average emissions from mineral plants is 10 tons/day or 3% of Basin emissions.

The remaining categories emit only 0.1% of Basin summer emissions and 1% in the winter. Annual emissions average only 0.3 tons/day or 0.1% of the Basin total SOx. This is less than the distributed small device emissions of 0.45 tons/day.

Detailed distributions of SOx sources for application categories by county are given in Table C-III for annual daily emissions.

In Los Angeles County the major SOx sources in order of importance are the utilities (winter), petroleum, coke-to-carbon processing, lead, glass, sulfuric acid, and plastics. Major Basin sources that are minor in this county include cement (none) and the iron and steel industries.

In Orange County the major application sources are utilities, oil field operations, aggregates, and glass. Riverside County has only one possible large source, cement manufacture, but, as mentioned elsewhere, SOx may be removed by particulates. San Bernardino County major sources are utilities, iron and steel, and, possibly, cement. Santa Barbara County shows only two sources in the South Coast Air Basin portion of the county and these are very minor sources of SOx. Ventura County has two major source categories; utilities and aggregates.

TABLE C-III

SOX PRELIMINARY INVENTORY BY APPLICATION CATEGORY AND COUNTY

ANNUAL AVERAGE DAILY SOX EMISSIONS, TONS/DAY AS SO₂

APPLICATION CATEGORY	L.A.	Orange	River.	San Bern.	San. Bar.	Ventura	Basin
I. UTILITY							
A. Gas turbine	0.03	0.01		--		--	0.04
B. Steam boiler	124.68	15.88		18.92		20.41	179.89
C. IC eng.-Nat. gas trans.	--	--			--	--	--
D. Standby turbine-Teleph.	--	--				--	--
II. INDUSTRIAL-CHEMICAL							
A. Agri. chem. & fertilizers	--	--					--
B. Plastics	0.17	--					0.17
C. Paints	--	--					--
D. Pharmaceuticals	--						--
E. Sulfuric acid	2.11						2.11
F. Coke/Carbon	28.01						28.01
G. Other	--		--				--
III. INDUSTRIAL-MFG, ASSEMBLY							
A. Heavy	--	--		--			--
B. Medium	0.02	--	--	0.01			0.03
C. Light	--	--	--	--		--	--
IV. INDUSTRIAL-METALS							
A. Iron & Steel	0.35			18.38			18.73
B. Aluminum	--		--			--	--
C. Lead and Other	8.64						8.64
V. INDUSTRIAL-MINERALS							
A. Asphalt	--		--	--	--	--	--
B. Cement and concrete	--		--	--	--	--	--
C. Glass	1.75	0.43	0.58	0.43			1.01
D. Mineral wool, insulation	0.04	--	--	--			2.18
E. Ceramics/Clay	0.01	--	--	--			0.04
F. Aggregate & Other		1.52		--		4.89	0.01
VI. INDUSTRIAL-PETROLEUM							
A. Field operations	--	6.61					6.62
B. Transport, storage	0.02	0.01				0.01	0.03
C. Refineries	93.63					0.04	93.67
D. Other	0.01						0.01
VII. INDUSTRIAL-AGRI & FOOD							
A. Canning, drying	0.01	--					0.01
B. Citrus	--	--	--	--			--
C. Sugar	--	0.01		--			0.01
D. Other	--	--		--			--
VIII. INDUSTRIAL-UNCLASSIFIED							
A. Food	--	--					--
B. Lumber	0.03			--			0.03
C. Other	0.13	--	--	--		--	0.13
IX. COMMERCIAL							
A. Office buildings	0.01	--					0.01
B. Process plants	--	--					--
C. Retail outlets	--	--					--
D. Other	--	--					--
X. INSTITUTIONAL							
A. Government	--						--
B. Hospitals	0.01	0.01		0.01		0.01	0.02
C. Penal Institutions	--		--	--		--	0.02
D. Education	0.05	--	--	--		--	--
E. Other	--			--			0.05
TOTALS	259.71	24.48	0.58	37.75	--	25.36	347.88

-- Sources present but less than 0.01 tons/day

5802-432

The emissions previously presented are based on total sulfur oxides expressed as SO_2 . Detailed distributions of the SO_2 and SO_3 components of these emissions were determined as part of the preliminary inventory but complete presentation will be deferred to the final report as significant changes in SO_3/SO_2 ratio are expected to result from the test phase of the program.

Basin total SO_3 emissions estimated for the summer, winter, and annual daily bases are 2.3, 15.3, and 9.2 tons as SO_3/day , respectively. These values compared with the total SOx rates of 159, 515, and 348 tons of SOx as SO_2/day represent conversion rates of 1.2, 2.4, and 2.1% by volume of SOx as SO_3 . A conversion rate of 3% was assumed for all fuel burning devices. The lower inventory values noted above are the result of unknown conversion rates for many material processing devices and for such devices a zero conversion rate was taken. Where specific source test data was available that data was used.

C-3.0 PRELIMINARY INVENTORY UNCERTAINTY

The assessment of inventory uncertainty is necessary to establish priorities for conducting the test phase of this program. As SOx emissions from fuel burning sources result from essentially complete conversion of fuel sulfur to SOx the uncertainty in these sources relates primarily to determination of the quantity of fuel burned. For the utilities, refineries and a large number of industrial plants, fuel use and sulfur content are reported on a daily or monthly basis to the local APCD. Therefore tests of these devices are not expected to result in significant improvement of the capability to properly inventory fuel burning devices. A greater uncertainty exists for material processing devices where part of the material sulfur may be released to form SOx and it is these sources toward which the test program is to be directed. Accordingly uncertainty assessment is considered only for the material processing devices.

Table C-IV lists the eleven major categories of material processing devices and indicates the annual average SOx emissions determined for the preliminary inventory of each category. Available emissions data from the LA APCD computer files, source tests of all APCD's and EPA tests, emission factors and inventories were compared as available for each source. Ranges of emissions based on lower and higher data were determined and the resulting percent uncertainty estimated as shown in the Table. These uncertainty values reflect only the differences found in the various sources of data. These differences may be due to actual equipment changes and do not necessarily reflect process variability.

The largest sources of SOx from material processing devices are the refinery fluid catalytic cracking units emitting 60 tons SO₂/day. Emissions for these units per barrel of oil processed vary by a factor of about 3 apparently reflecting different crude stock sulfur content and unit operation. Indications are that emissions could be lower than the preliminary inventory value by as much as 22 tons/day (-37%).

TABLE C-IV

SO_x SOURCE UNCERTAINTY
FOR MATERIAL PROCESSING OPERATIONS

		Annual Average SO _x Emissions, Tons SO ₂ /day	Estimated ^{**} Uncertainty, Tons SO ₂ /day	Estimated ^{**} Uncertainty, Percent
1.	8 Refinery fluid catalytic cracking units	60	+10 -22	+17 -37
2.	5 Petroleum coke kilns	28	+11 -10	+39 -36
3.	20 Refinery sulfur recovery plants with 12 tail gas units	20	+ 3 - 9	+15 -45
4.	17 Steel operations	17	+ 9 - 4	+53 -24
5.	10 Lead furnaces	9	+ 7 - 2	+78 -22
6.	5 Sulfuric acid plants	2.3	+14 - 0.4	+600 -17
7.	9 Oil field vapor phase	6.6	+ 2 - 4	+30 -60
8.	7 Aggregate kilns	6.4	+ 1	+16
9.	25 Glass furnaces	2.2	+ 2.5 - 1.5	+114 -68
10.	1 Brake shoe debonder	.12	+ 0.03	+25
11.	4 Gypsum/rockwool furnaces	.03	+ 0.01	+33
TOTAL		153	+23 *	+15

* Root mean square of individual uncertainties with average of + and - values

** Uncertainty reflects only differences in the various sources of data and not necessarily process variability.

The largest uncertainty was found for the sulfuric acid plants (+600%). This is related primarily to the unknown status of emissions control units installed on these devices with respect to equipment installation dates and reported performance. As these units are reported to be operated at full capacity year round it is expected that tests will easily resolve the uncertainty. A high positive uncertainty exists for glass furnaces although the absolute level of emissions is relatively low. Variations in the furnace charge compositions is believed to be the main source of uncertainty. Salt cake (Na_2SO_4) is the major material source of SO_x in glass furnaces and is charged at the rate of about 6 pounds per ton of total charge (sand, soda ash, lime, etc.). Variations in the charge formula necessary for different types of glass must be determined for the inventory period and emissions related to salt cake charge rate in order that the uncertainty can be reduced. The uncertainty in all material processing devices is sufficiently high so that one or more of each device should be tested to resolve these questions.

The total annual emissions for all material processing devices, as shown in the table, is 153 tons of SO_x /day. This amount is nearly equal to the summer daily Basin average previously presented. Seasonal variations in these devices are relatively minor and the Basin total 159 tons of SO_x per day reported for the summer is essentially due to material processing.

REFERENCES

1. Bartz, D. R., et al., "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin of California," KVB Engineering, ARB-R-2-1471-74-31, PB-237688/7WP, Sept. 1974.
21. Los Angeles County Electric Utility Power Plant Fuel Use and Emissions for August 1972 - December 1974, LAC APCD.

Blank Page

APPENDIX D

SOURCE TEST METHODS AND RESULTS

TABLE OF CONTENTS

	<u>Page</u>
D-1.0 INTRODUCTION	D-1
D-2.0 SO _x WET CHEMICAL METHODS	D-2
D-3.0 EXPERIMENTAL EQUIPMENT AND PROCEDURES	D-6
D-4.0 DATA REDUCTION - SO ₂	D-14
D-5.0 DATA REDUCTION - SO ₃	D-23
D-6.0 SUMMARY OF TEST RESULTS	D-26
REFERENCES	D-29

Blank Page

APPENDIX D

SOURCE TEST METHODS AND RESULTS

D-1.0 INTRODUCTION

The experimental field test program extended from May 5 until July 21, 1975. During this period measurements were made to determine the emission rates from a total of thirty-eight devices. The purpose of these measurements was to:

1. Determine SOx emissions from major industrial devices that process sulfur-bearing materials in the South Coast Air Basin to resolve uncertainties in existing data.
2. Relate the SOx emissions to process rates so that emission factors can be developed for application to untested devices and improve the predictive capability for assessment of seasonal and capacity variations.
3. Obtain sufficient operational process data on the various devices to enable an assessment of potential emissions reduction by existing technology.

It was first necessary to determine those potential SOx sources within the basin for which both the amount of SOx emitted and the uncertainty of the available information describing those sources was significant. These questions were both answered during the preliminary inventory phase of the program. Plant operators of potential test sites were then contacted and the plants were visited to make a further evaluation of the desirability of performing field test measurements. If it was determined that a field test would provide useful information a test date(s) was scheduled and arrangements were made for electrical power, working space, and other operator assistance as might be required.

D-2.0 SOx WET CHEMICAL METHODS

Sulfur is usually emitted from stack gases in the form of either SO_2 or SO_3 (SOx). In some cases hydrogen sulfide (H_2S) is present and at other times small amounts of carbon disulfide (CS_2) and carbonyl sulfide (COS) are emitted (tail gas units of Claus plants). The sulfur emissions of interest in this program, however, are the sulfur oxides (SOx) and these are 90-99 percent SO_2 . When measurements on total SOx emissions, only, are desired, it is not necessary to isolate that part of the emission that is SO_3 (H_2SO_4 mist) from that which is SO_2 . The measurement problem is then simplified considerably.

Sulfur dioxide (SO_2) in stack gases can be measured by either instrumental or wet chemical methods. Measurements for SO_3 must be obtained using wet chemical collection and analysis methods. Although SO_3 can, in principle, also be measured instrumentally, a combination sampling and analysis system is not yet available. Measurements for this species have, in the past, been completely dependent upon the results of wet chemical methods.

The problem that must usually be faced when analyzing stack gases for sulfur oxide emissions, is how to successfully isolate and collect SO_2 and SO_3 in the presence of other interfering substances. Once this has been done the laboratory techniques employed for measuring the quantities of SO_2 and SO_3 that are present are usually satisfactory (Ref. 43). Therefore although the various methods that have been used for SO_2/SO_3 analysis of stack gases may utilize different chemical analytical procedures, the sampling procedures represent the critical step in the success of the various methods and also account for the most important differences in the results (Ref. 43, 44). Three different methods will be discussed below.

EPA Method 8 (Ref. 45). The EPA has proposed Method 8 as a means of measuring sulfuric acid mist (SO_3 or H_2SO_4) and SO_2 emissions. This method employs standard Greenburg-Smith impingers so that sampling can be performed isokinetically as is required when a significant portion of the acid mist particles that are collected are larger than 3μ (Ref. 46, 47). For most SO_x emission sources, however, isokinetic sampling is not necessary. The collecting solutions that are used in Method 8 are an 80 percent iso-propanol solution in water for SO_3 in the first impinger followed by two impingers charged with 3 percent solutions of H_2O_2 to collect SO_2 . The iso-propanol solution, while collecting the SO_3 , presumably inhibits the oxidation of any SO_2 which might also have dissolved. On completion of sample collection, the SO_2 is then purged from the SO_3 collector by a stream of air and transferred to the H_2O_2 solution which follows.

There is evidence, however, that the iso-propanol does not completely inhibit the oxidation of the SO_2 , and that the SO_2 may not be completely purged from the SO_3 collection solution. This has been shown by collaborative laboratory test results using midget (EPA Method 6) impingers rather than the standard impingers of EPA Method 8. These tests showed that the SO_2 retained by the IPA solution may be as much as 2.5 percent of the total SO_2 present in the sample gas (Ref. 48). The average SO_2 retained was slightly less than 1 percent of the SO_2 when concentrations of 397 and 707 ppm SO_2 were used.

Collection of SO_3 in the EPA Method 8 depends upon the absorption of some of the SO_3 in the solution of the first impinger and on the hydrolysis to H_2SO_4 mist of the remaining SO_3 . The mist that is generated is then collected on a glass fibre filter which follows the SO_3 impinger. The efficiency of this particular arrangement for collection of the H_2SO_4 mist has not yet been fully documented.

Tests conducted to verify the collection efficiency of SO_2 and SO_3 by EPA Method 8 have been inconclusive (Ref. 49), and more involved testing is apparently necessary to verify the limits of collection efficiency for this method (Ref. 50). In other tests (Ref. 51), however, the SO_2 collection efficiency of the midget impinger has been shown to be 90-95%.

Shell Method (Ref. 30). The Shell-Emeryville method uses the same chemicals as the EPA Method 8. Ninety percent iso-propanol solutions are used to collect SO_3 and an H_2O_2 solution follows for collecting SO_2 . Rather than impingers, however, lamp sulfur absorbers with coarse frits are used. The absorbing solutions for this method suffer from the same criticisms as those used in EPA Method 8, however, the efficiency of the SO_3 absorbers seems to be somewhat better than that observed with EPA Method 8 (Ref. 52). Isokinetic sampling generally is not possible with the Shell-Emeryville train, and for this reason this method may not be useful for sulfuric acid plant testing. A fibre glass filter is placed in the sampling probe to remove the solid particulates which could cause either or both anion and cation interference with the analytical procedure. The SO_3 results obtained by this procedure may be somewhat high because of problems associated with the use of the IPA solution. The method is easy to use and KVB has had considerable experience with it.

LA APCD Method (Ref. 31). In this method, H_2SO_4 mist particles are collected on a Whatman thimble paper filter prior to absorbing SO_2 in a solution of 5% NaOH. The thimble is maintained at 165-200°F to prevent the condensation of water vapor, but yet permit the collection of condensed H_2SO_4 mist particles. The apparent weakness in this method is that there is no convincing evidence by which to evaluate the efficiency of the paper filter as a means of collecting SO_3 . The reaction of SO_3 with H_2O and the subsequent aggregation of the H_2SO_4 molecules to form mist particles is a dynamic process. In some test situations this dynamic process may not have progressed to the point where the paper thimble filter can serve as an effective separation device. The SO_3 results obtained by this method in practice have not always been consistent (Ref. 53). A similar conclusion has been reached in regard to a second controlled condensation method (Ref. 43, 54). Although incomplete aggregation of H_2SO_4 mist particles has not been shown to be a problem, this could be a weak point in the method. Because of this, SO_3 measurements made by this method are believed to be on the low side. It is possible to sample

isokinetically with this method but the laboratory analytical procedures require significantly greater effort than the simple titration procedure of the previous methods.

D-3.0 EXPERIMENTAL EQUIPMENT AND PROCEDURES

From the above discussion, it is not clear that one method is superior to the others. Each appears to have a weakness in spite of the several development programs that have been pursued in recent years by the EPA and others. For the current program the Shell method was selected as the primary method because (a) it was believed best suited for test conditions expected, (b) KVB had most experience with this method and (c) it required the minimum cost and manpower to complete a given test from sampling in the field through laboratory analysis. The latter criteria was important as once the test program was started, a new device would be tested every day. Replicate samples had to be analyzed which would result in a large number of chemical analyses.

As all regulatory agencies within the South Coast Air Basin have adopted the LA APCD method for their own purposes, it also seemed advisable to include some field tests with the LA APCD method. This was to ensure that the results obtained by the two methods would provide equivalent results or, at least, to determine the nature of the discrepancies if any should arise.

Back-up instrumental measurement of SO_2 also seemed prudent for several reasons. It was known that SO_2 would comprise in excess of 90 percent of the total SO_x emissions. Therefore, a back-up instrumental measurement for SO_2 seemed desirable even if one for SO_3 was not available. Results from wet chemical analysis would not be available for, at times, several days after a field test was completed. Immediate knowledge of SO_2 concentration in the effluent gas, especially for sources for which previous data was not available, would be helpful in determining sample collection times required for the wet methods. It would also help to screen those sources with very low SO_2 emission rates and for which wet chemical tests would not contribute to significant improvement in inventory verification.

As the test program was to emphasize industrial devices that processed sulfur-bearing materials rather than combustion devices, it was anticipated that the SO_2 concentration in the effluent streams might reflect the cyclical nature of the process when such existed. When that was the case it would be important to define the nature of these periodic cycles and to account for them in arriving at the appropriate emission factor.

Table D-I lists the variables which were measured and indicates the methods that were used. Two Teledyne instruments provided continuous strip chart indication of the O_2 and SO_2 to evaluate process fluctuations and cycles. The two wet chemistry methods provided results for SO_2 and SO_3 .

Stack flow rate was considered to be more difficult to ascertain for non-combustion than combustion devices. Calculations based on fuel flow and oxygen content frequently used for combustion devices are less certain and sometimes not available where materials are processed. Some of the chemicals may also react to influence the stoichiometry. Where sufficient information was available process calculations were performed in order to check stack effluent rates as determined from pitot tube measurements.

Process material flow rates were obtained and samples of pertinent materials were analyzed for sulfur content. The process rate was not always available, and when this was the case the device design rating was reported instead.

The test instruments were installed in a test van which could be readily moved to each new test site. The instrument package was mounted on a work bench which also provided desk space. The various equipment and supplies associated with the two wet chemical methods for SO_x analysis required considerable storage space. A 150' heated line to transport the stack sample to the instrumental package was mounted on a rack on the exterior of the test van.

TABLE D-I

MEASURED VARIABLES AND INSTRUMENTS

Variable	Instrument or Method
1. Oxygen	Teledyne Analytical Instruments Oxygen Analyzer Model 326A
2. Sulfur Dioxide (SO ₂)	1. Shell-Emeryville (H ₂ O ₂) 2. LA APCD (NaOH) 3. Teledyne Analytical Instruments Series 600 Photometric SO ₂ Analyzer
3. Sulfur Trioxide (as SO ₃ and H ₂ SO ₄)	1. Shell-Emeryville (IPA) 2. LA APCD (dry filter)
4. Exhaust Gas Flow Rate	Combination of (1) and process flow rates (or) pitot tube and thermo- couple probe
5. Exhaust Gas Temperature	Operator Data (or) Thermocouple probe
6. Process Material Flow Rate	Operator Data
7. Process Material Sulfur Content	Laboratory analysis of sample
8. Exhaust Gas Moisture content	LA APCD impinger Condensable water vapor train method

A schematic diagram of the instrument console for the continuous sampling of O_2 and SO_2 is shown in Figure D-1. Quartz and pyrex probes were used to withdraw the samples from the stack. The sample then passed through a 150 foot heated sample line on the way to the instrument console. The SO_2 instrument measured SO_2 on a wet basis so that heating was provided for the entire sample path from stack to instrument. Oxygen content was measured on a dry basis and provision for water extraction was included.

The test apparatus for the Shell-Emeryville method is shown in Figure D-2. It is mounted in a portable box that can be located within 5 feet of the sample port. Three identical boxes were constructed to facilitate field operations. Apparatus for the LA APCD back-up method for SO_2/SO_3 is illustrated in Figure D-3. This apparatus is also portable. Heated pyrex probes were used with both methods to prevent condensation. When stack gas temperatures exceeded $1000^\circ F$ the pyrex probes were replaced with quartz probes.

The basic field test procedures are summarized below:

1. Turn on instruments and heated line.
2. Install heated line on stack and transport wet chemistry apparatus to sampling port. Existing sampling ports are to be used.
3. Allow continuous SO_2 and O_2 instruments to stabilize for 2 hours from cold start or $1/2$ hour from standby.
4. Calibrate the continuous SO_2 and O_2 instruments with standard nitrogen for zero, span gas for SO_2 and ambient air for oxygen. Repeat calibration until zero and span readings are unchanged on both instrument meters and recorder.
5. Maintain continuous strip chart recording of SO_2 and O_2 during all wet chemistry sampling and note sample times on recording.
6. Recheck instrument calibrations every 30 minutes or prior to each data recording.

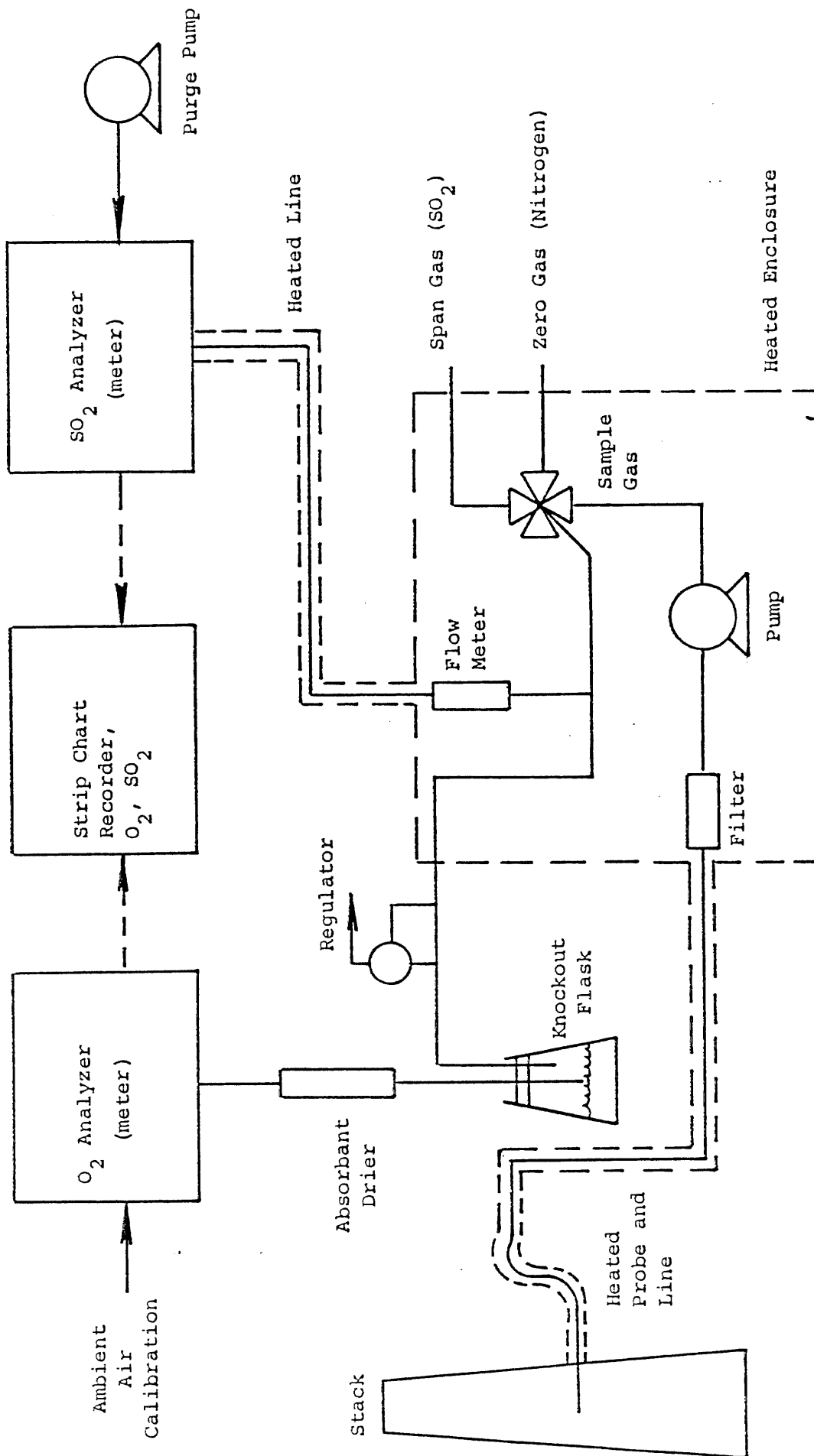


FIGURE D-1. CONTINUOUS MONITORING INSTRUMENT SCHEMATIC FOR STACK SAMPLING OF O₂ AND SO₂.

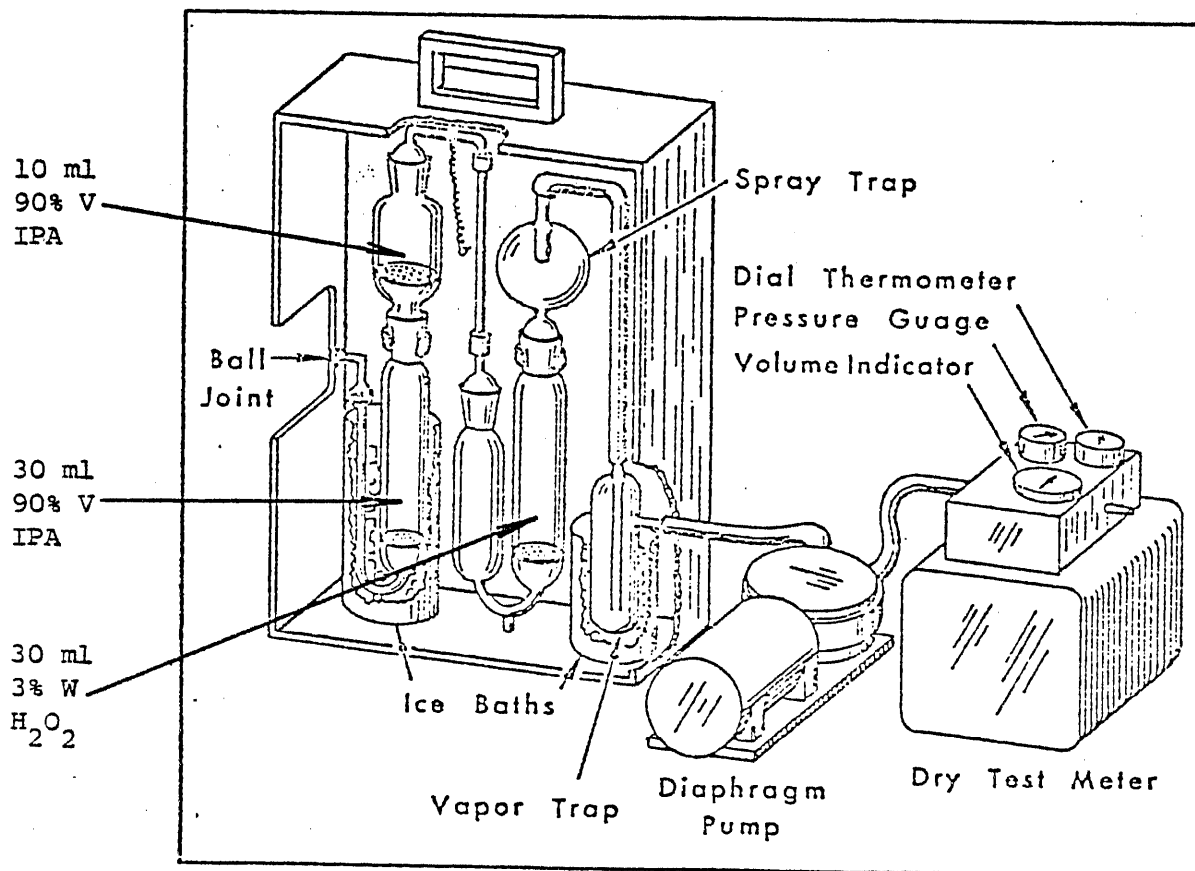
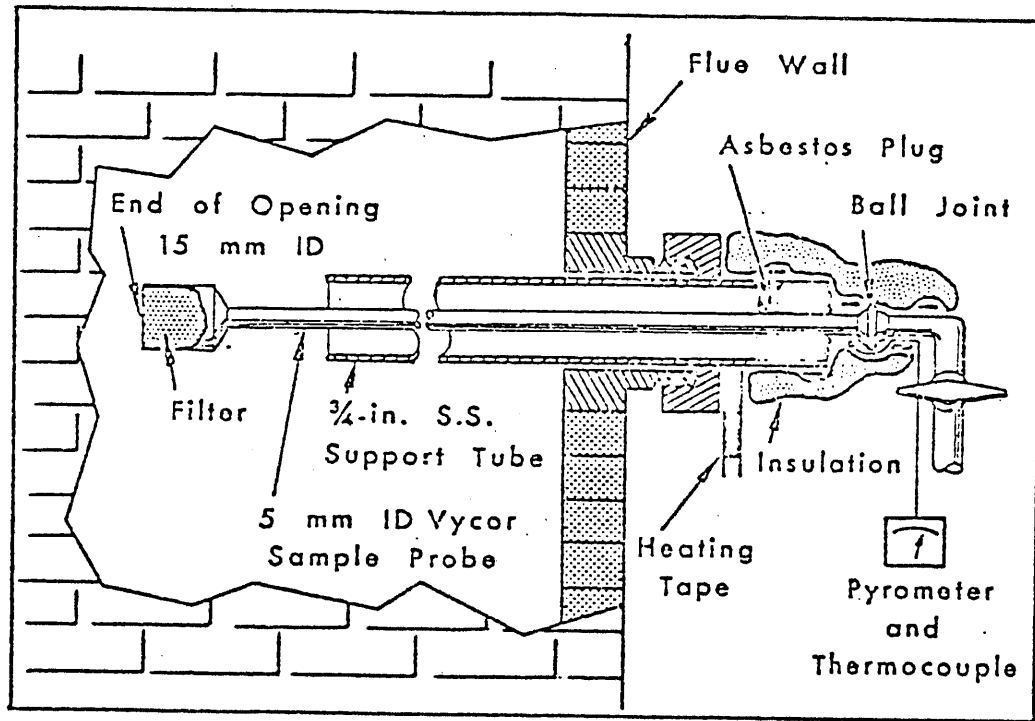
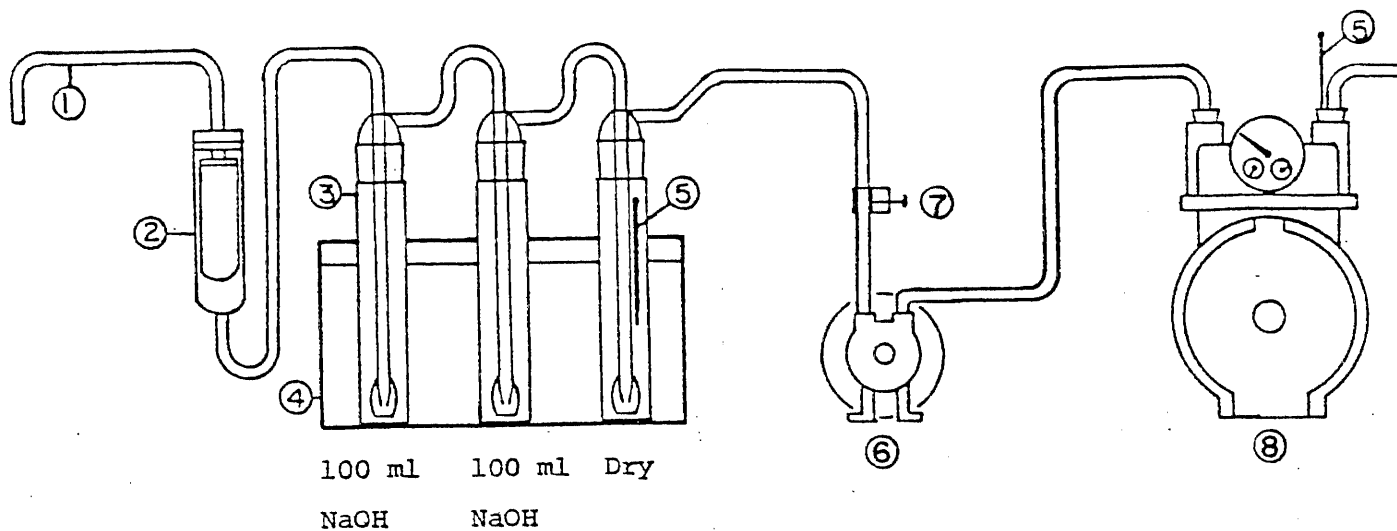


FIGURE D-2. SCHEMATIC OF SHELL-EMERYVILLE SAMPLING TRAIN FOR WET CHEMISTRY MEASUREMENT OF SO_2 AND SO_3 .



1. SAMPLING PROBE, PYREX OR QUARTZ
2. WHATMAN DRY FILTER
3. IMPINGERS
4. ICE BATH CONTAINER
5. THERMOMETER
6. VACUUM PUMP
7. HOSE CLAMP TO CONTROL GAS FLOW RATE
8. DRY GAS TEST METER

FIGURE D-3. SCHEMATIC OF LA APCD SAMPLING TRAIN FOR WET CHEMISTRY MEASUREMENT OF SO_2 AND SO_3 .

7. Obtain a minimum of three samples with the Shell method in accordance with the Shell procedure (Ref. 30).
8. At selected sources obtain samples with the LA APCD method in accordance with the LA APCD Source Test Manual (Ref. 31).
9. Obtain stack gas velocity data with the pitot tube traverses.
10. Obtain stack gas moisture content with the condensible water vapor train.
11. Obtain and record all pertinent process data sufficient to define operating capacity and process variables during the period of wet chemistry sampling.
12. Obtain samples of process materials for laboratory analysis.
13. Upon test completion, purge the instruments and shut down or place in standby condition. Prepare all wet chemistry samples for delivery to the laboratory for analysis.

D-4.0 DATA REDUCTION - SO₂

In most cases the SO₂ concentration varied somewhat as a function of time. In general, however, these variations occurred within cyclic time periods of several minutes or in some cases as much as a half hour. If this was the case the periodic changes were automatically averaged by the wet chemical methods used. The sampling period for the wet chemical method ranged between 40-60 minutes. A process in which changes occurred over significantly longer time intervals for example is that of the steel open hearth furnaces. The process cycles were approximately 8 hours in length.

Figure D-4 shows the results of instrumental and wet chemical analysis for a stack effluent having a stable level of SO₂ concentration. A significant instrumental drift is apparent, however, and this was corrected periodically with zero and calibration checks. In determining the average instrumental reading for a given time period this zero drift was taken into account. The LA APCD wet chemical method was used and in this case the ratio of instrumental/wet chemical analysis for SO₂ was 0.98, 1.01, and 1.03, respectively for the three wet chemical tests.

Sulfur dioxide and oxygen traces resulting from the analysis of stack gas from a sulfuric acid plant are shown in Figure D-5. The lower curve is for SO₂ and indicates an average of about 470 ppm (wet). The oxygen concentration was approximately 15 percent. For this test the LA APCD wet method was used and the results of these tests are plotted at the appropriate time period. The average value for the SO₂ instrumental analysis for the same time period is also plotted. The latter was determined geometrically by equating the areas above and below the chosen average value. In this test the ratios of the instrumental/wet chemical results were 0.96, 0.96, and 1.09 for time periods 1, 2 and 3 respectively. Also shown on the plot are individual data points for SO₂ concentration as determined by separate instrumental analysis by the plant operator.

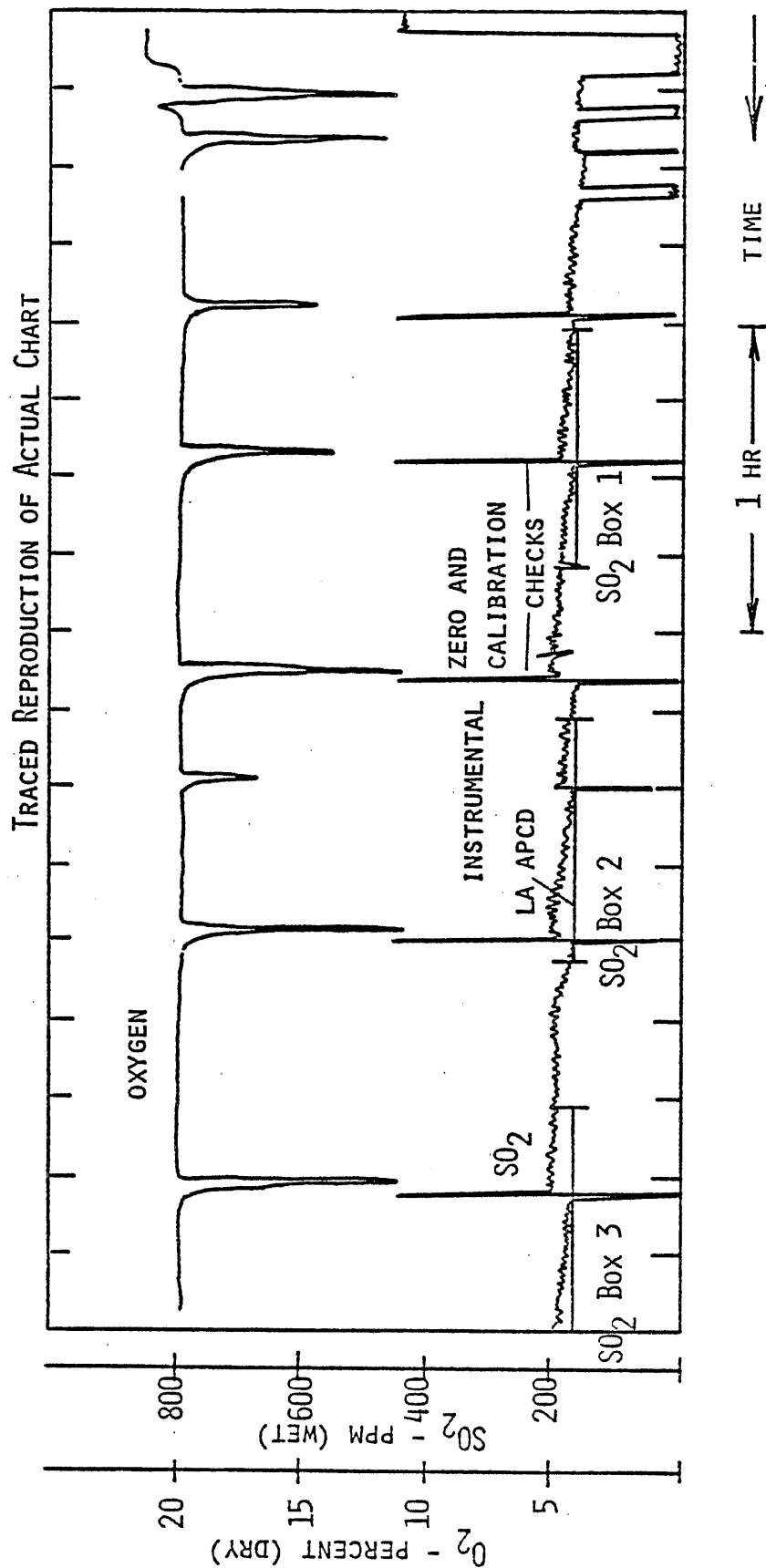


FIGURE D-4. SULFUR DIOXIDE AND OXYGEN RESULTS FOR EMISSIONS FROM WELL-HEAD INCINERATOR.

5802-432

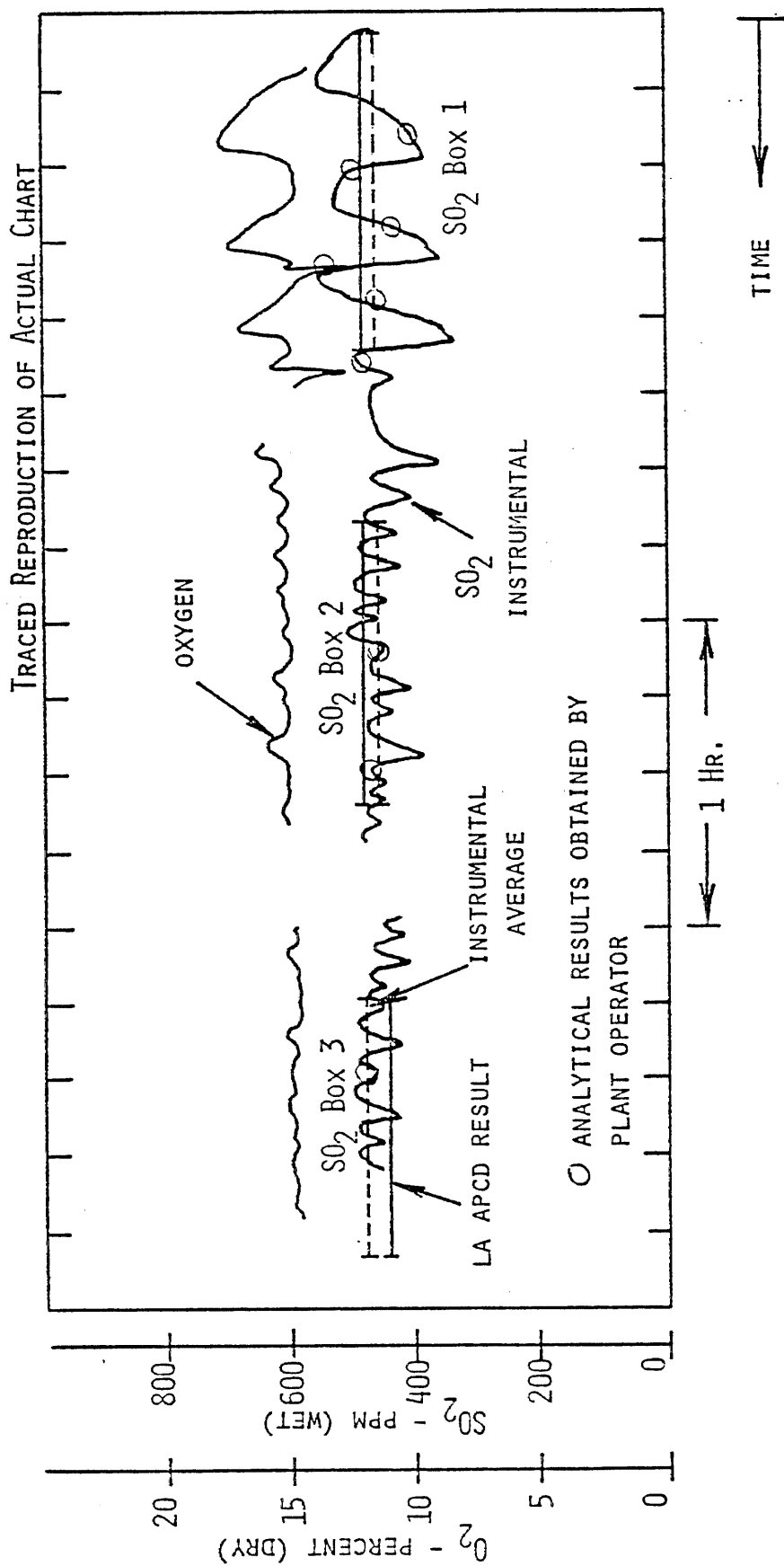


FIGURE D-5. SULFUR DIOXIDE AND OXYGEN RESULTS FOR EMISSIONS FROM A SULFURIC ACID PLANT.

5802-432

In Figure D-6 is an example of a process for which the SO_2 concentration was fairly stable in the short term but for which a single large excursion occurred once every twenty-four hours. The excursion lasted for a period of about two hours and then returned to the base level where, presumably, it remained until the following day when the process cycle that had caused the excursion was repeated. The Shell wet chemical method was used for this test and those results are shown on the figure along with the average meter reading. The instrumental/wet chemical ratios were 1.18, 1.02, and 1.06. To determine total SO_x emissions from a source such as this one, the average cycle emissions over a twenty-four hour period was calculated.

The measured SO_2 concentration emerging from the tail gas unit of a sulfur plant is illustrated in Figure D-7. The first part of the trace shows both high and highly variable concentrations of SO_2 . A process adjustment (leaking valve tightened) was then made, and the SO_2 concentration level immediately dropped to ~100 ppm. The results of two wet chemical results obtained with Shell method are also shown.

Comparisons of instrumental SO_2 versus wet chemical SO_2 results for the Shell and the LA APCD methods are shown in Figures D-8 and D-9. In Figure D-8 a consistent trend is apparent which shows that the results for the Shell wet chemical method are about 9 percent lower than the instrumental reading for SO_2 . Almost all of the points are above the 45° diagonal. In a similar plot for the LA APCD method, no such trend is apparent and the agreement between the instrumental and wet chemical method appears more satisfactory. A statistical reduction of the Shell data, excluding the three low points at 190 ppm, showed the mean instrumental/wet measurement ratio to be 1.088. There was a ninety percent probability that this ratio would lie between 0.97 and 1.21 for any particular experimental measurement. This result is in agreement with test results obtained previously by collaborative testing of EPA Method 6 (H_2O_2 solution with small impingers) (Ref. 51). It was reported there that SO_2 values between 5 and 10 percent below true values were found. The wet chemical methods were also checked by absorbing measured quantities

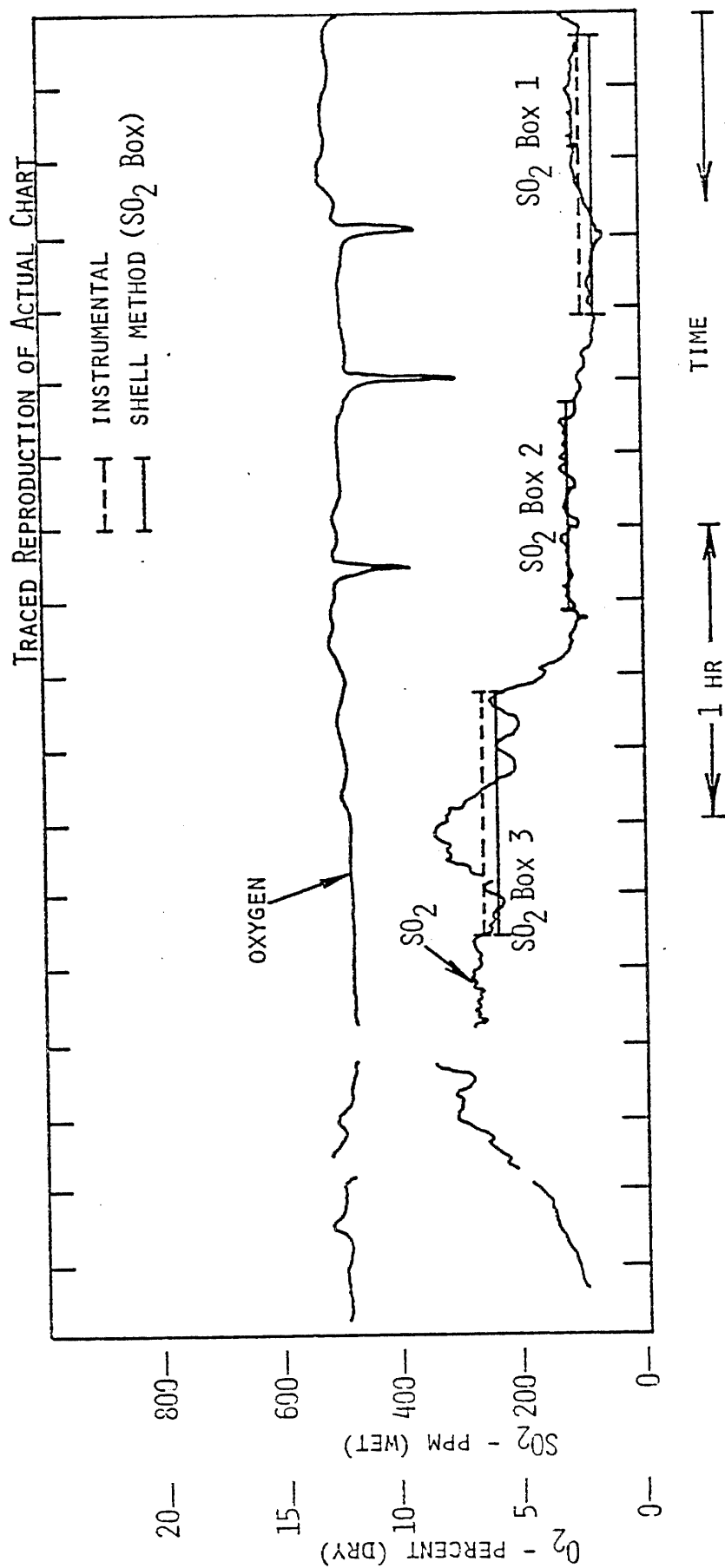


FIGURE D-6. SULFUR DIOXIDE AND OXYGEN RESULTS FOR EMISSIONS FROM PROCESS UNIT EXHIBITING EMISSION EXCURSION ONCE EACH 24-HOUR PERIOD.

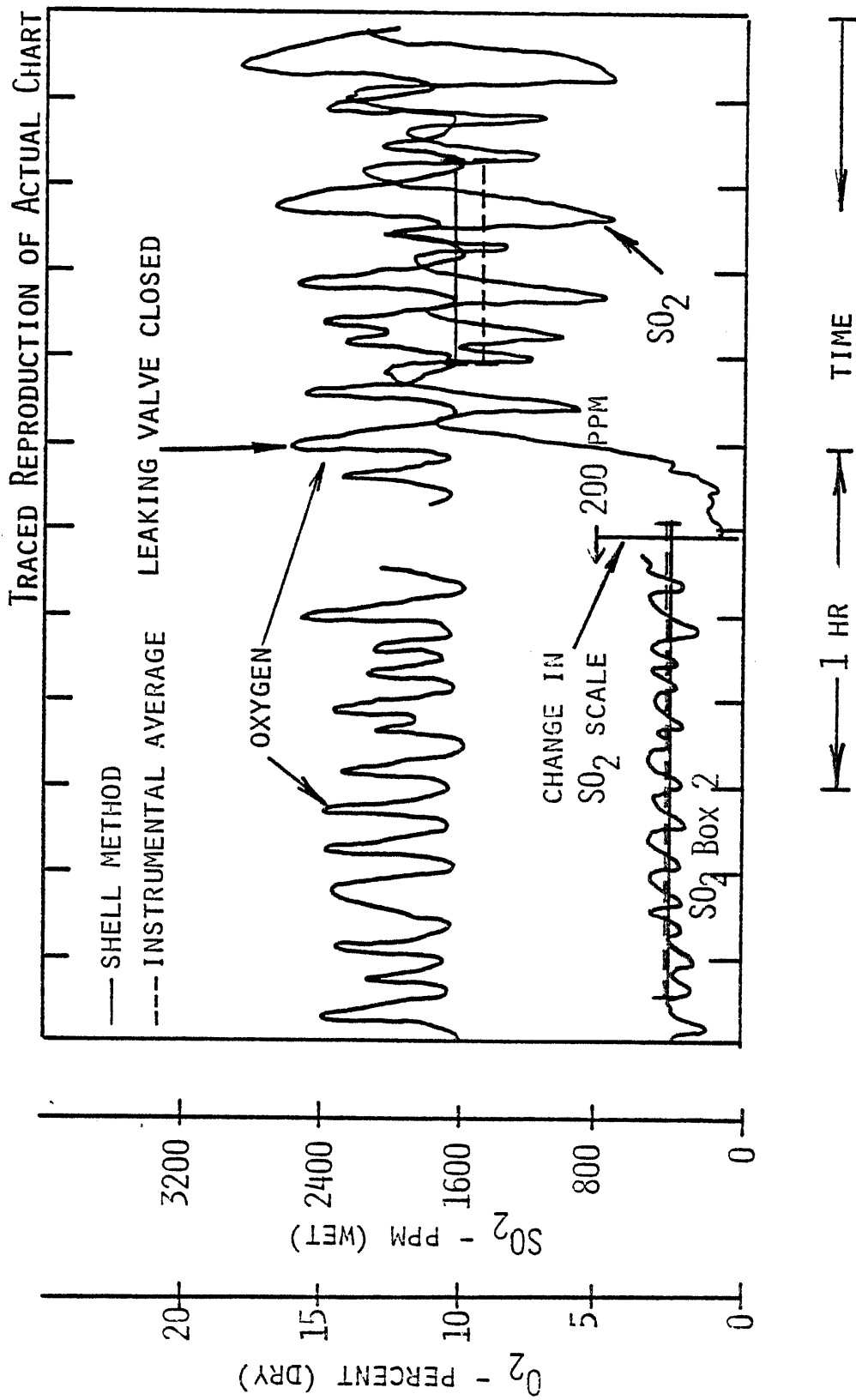


FIGURE D-7. SULFUR DIOXIDE AND OXYGEN RESULTS FOR EMISSIONS FROM TAIL GAS UNIT OF SULFUR PLANT.

5802-432

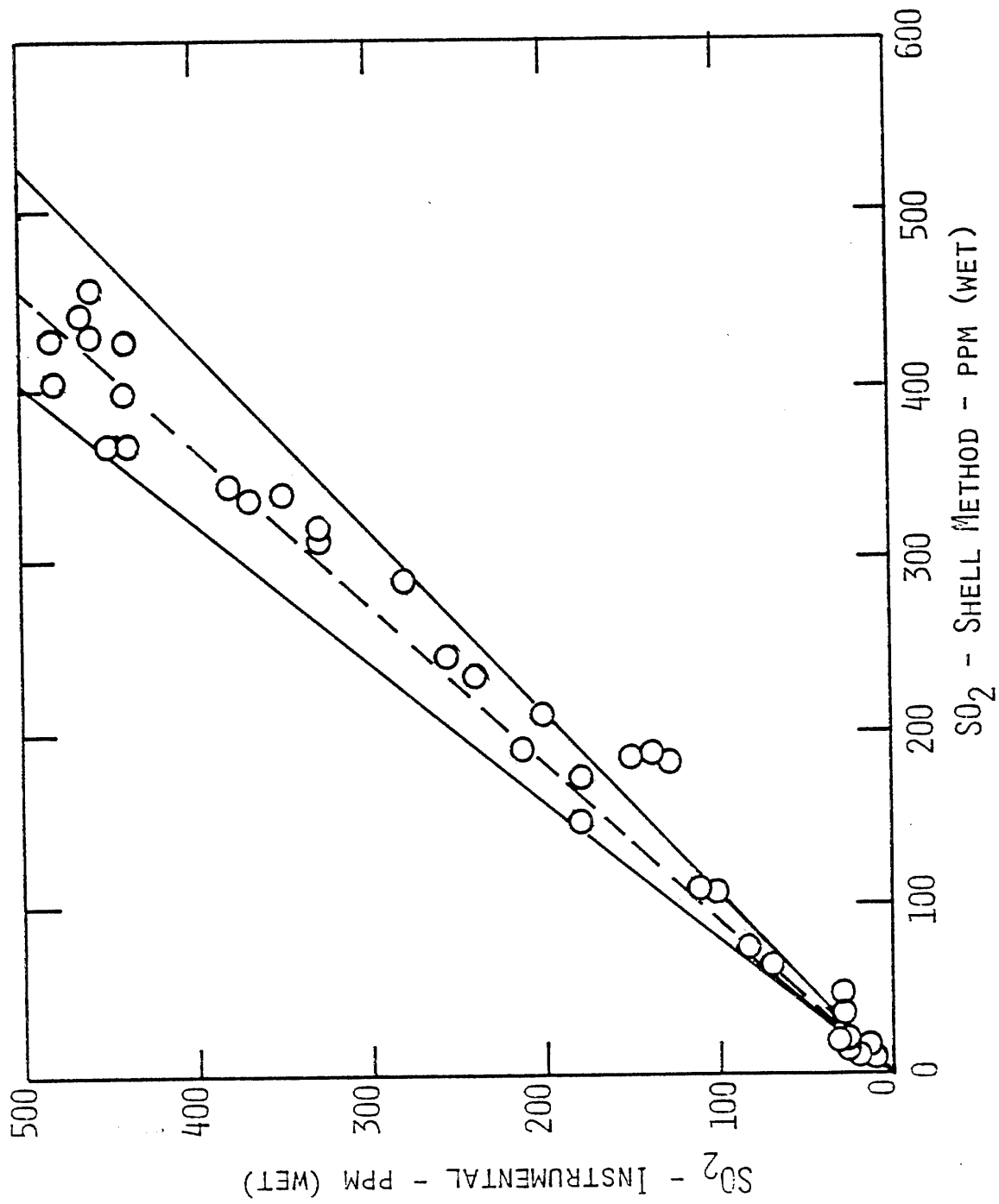


FIGURE D-8. COMPARISON OF SO₂ INSTRUMENTAL AND SO₂ SHELL METHOD RESULTS

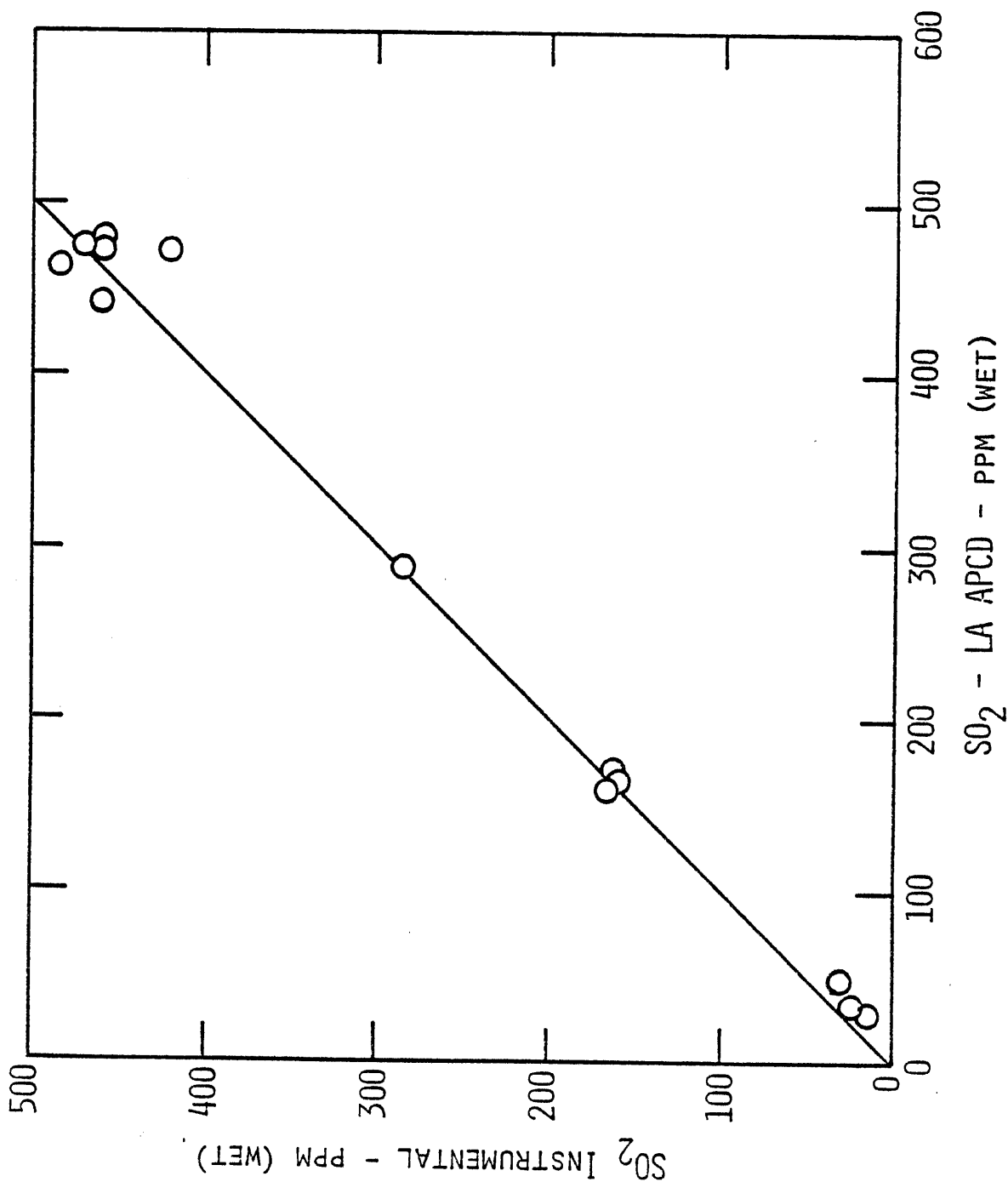


FIGURE D-9. COMPARISON OF SO₂ INSTRUMENTAL AND SO₂ LA APCD METHOD RESULTS.

of the certified SO₂ calibration gases employed for calibrating the ultraviolet analyzer. Results for SO₂ using the Shell method were 5-6 percent low in those tests also. Therefore in employing the field test results for SO₂ as measured by the Shell method, the average instrumental/wet method ratio of 1.088 was used to correct the measured values by the Shell method to one more in agreement with the other methods of measurement.

Wet chemical analyses were obtained at all test sites with one exception. Instrumental readings for SO₂ concentration were obtained at most, but not all test sites. The SO₂ concentrations reported are based on wet chemical results. When the Shell method was used, the measured value was multiplied by a factor of 1.088 to obtain the reported ppm of SO₂. When the LA APCD method was used, those results for SO₂ were reported directly. The results for the replicate (normally three) wet chemical analyses were averaged to obtain the reported value.

D-5.0 DATA REDUCTION - SO₃

SO₃ results were available only from the results of wet chemical analyses. Experimental results for the tests employing the Shell method are summarized in Figure D-10. For tests where the total SOx concentration was greater than 50 ppm, there was only one case where the percentage SO₃/SOx ratio was as much as 10%. For that particular device, a value of 10% is not unreasonable. In three other cases the percentage SO₃ was greater than 4%. It was 4 or less for all other cases where the total SOx was greater than 50 ppm. At total SOx values less than 50, however, the percentage SO₃ was greater than 10 in most cases and in some cases greater than 20%. These excessively high values are believed to be related to the limited amount of SO₂ that is dissolved in the isopropyl alcohol solutions and which is not removed (see above and Ref. 74) by purging. This residual SO₂ remains to be measured as SO₃. Of course, the smaller the total ppm of SO₂ in the sample gas the more important this residual SO₂ could become. Results similar to those in Figure D-10 have also been obtained for combustion processes (see Figure G-1).

Although it is not clear at what point the residual SO₂ may become important in determining the reported SO₃ concentrations, it seems that below total SOx concentrations of 50-100 ppm the reported SO₃ concentrations should be viewed with some skepticism.

The SO₃ experimental results for the Shell and LA APCD method that were obtained on common tests are shown on Figure D-11. Points for total sulfate which were obtained with the LA APCD method are also shown. SO₃ results measured by the LA APCD method were as high as those measured with the Shell method in only one case. In all other cases they were lower. These results are consistent with previous discussion where it was indicated that SO₃ results obtained with the Shell method might be high, especially at low total SOx, and that the SO₃ results obtained with the LA APCD method would be low, if anything. The amount of data obtained is insufficient to determine which method, in fact, records the more accurate values of SO₃. Both methods suffer from a lack of adequate calibration procedures.

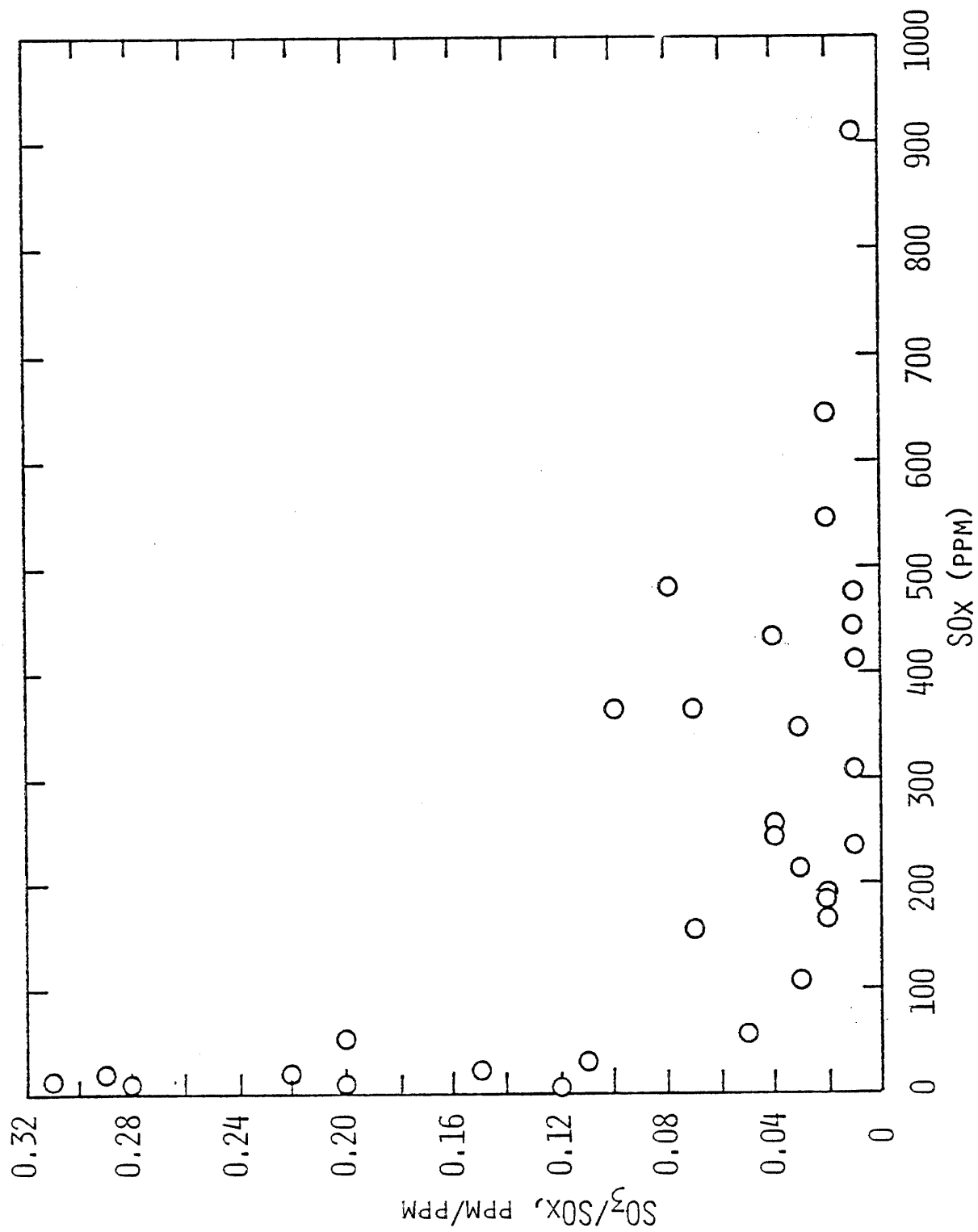


FIGURE D-10. SO_3 EXPERIMENTAL RESULTS OBTAINED WITH SHELL METHOD.

5802-432

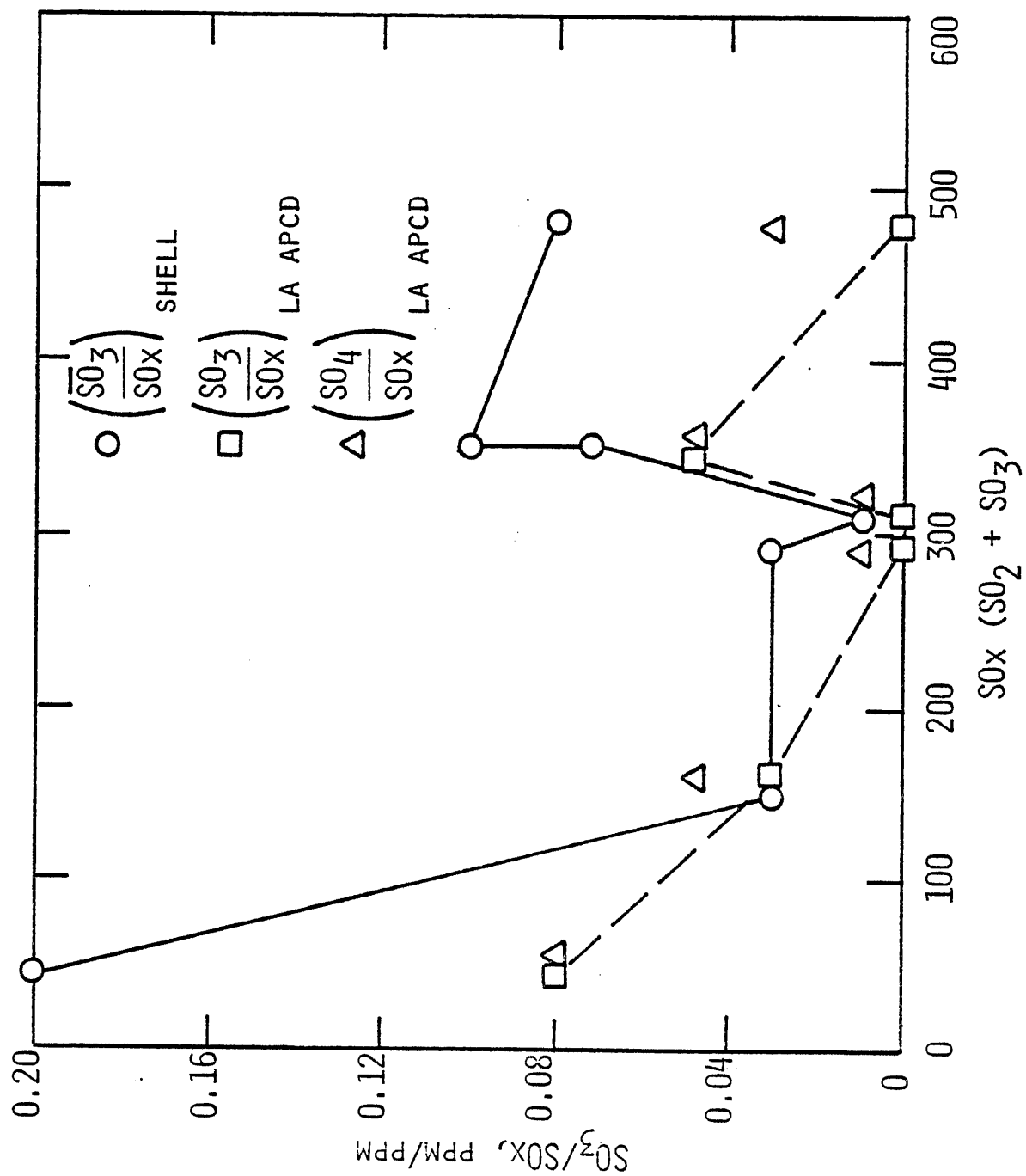


FIGURE D-11. COMPARISON OF SO₃ EXPERIMENTAL RESULTS FOR SHELL AND LA APCD METHODS.

5802-432

D-6.0 SUMMARY OF TEST RESULTS

The measured SOx concentration levels, stack gas effluent rates and calculated emission rates are summarized in Table D-II. Emission rates were calculated based on measured wet stack gas flows and wet basis SOx concentration levels where

$$M_{SO_2} = (10.1)(10^{-6}) \cdot C_{SO_2} \cdot Q$$

$$M_{SO_3} = (12.7)(10^{-6}) \cdot C_{SO_3} \cdot Q$$

M = emission rate lb/hr

C = concentration ppm (wet)

Q = stack effluent rate SCFM (wet)

The estimated random factor uncertainties in measurements and calculated values are:

Measured values:

Stack flow rate, SCFM (wet)	+ 10%
Stack gas moisture content	+ 5%
Meter SO ₂ concentration, ppm (wet)	+ 2%
Shell SO ₂ concentration, ppm (dry)	+ 5%
LA APCD SO ₂ concentration, ppm (dry)	+ 3%
Shell SO ₃ concentration, ppm (wet)	+ 20%
LA APCD SO ₃ concentration, ppm (wet)	+ 20%

Derived values:

SO ₂ concentration, ppm wet	+ 9%
SO ₃ concentration, ppm wet	+ 21%
SO ₂ emission rate, lb/hr	+ 13%
SO ₃ emission rate, lb/hr	+ 24%

Non-random method bias for the two SO₃ methods may contribute to a higher uncertainty in SO₃ emissions, but this could not be determined.

TABLE D-II
TEST DATA SUMMARY

Test No.	Device Type	Process Rate	Stack Flow SCFM (wet)	Stack Gas % O ₂ (dry)	Stack Gas % H ₂ O (vol.)	SO ₂ , ppm (wet)	SO ₃ , ppm (wet)	SO ₂ /SO ₃ % (vol.)	Emission Rates SO ₂ lb/h	Emission Rates SO ₃ lb/h	SO _x Test Method
1	Glass Furnace	239 t/d	22,000	8.0	9.0	259.	8.	3.0	57.6	2.22	Shell
2-1	Glass Furnace	240 (1) t/d	23,000 (8)	9.0	9.0 (8)	21.	3.0	12.7	4.8	0.9	Shell
2-2	Glass Furnace	195 (1) t/d	13,000 (8)	--	--	11.	4.6	29.5	1.4	0.8	LA APCD
3	Glass Furnace	77 t/d	11,443	11.0	11.0	139.	9.0	6.1	16.1	1.3	Shell
4	Sulfuric Acid Plt.	450 (1) t/d	25,510	8.4	1.0	248.	3.0	1.2	63.9	1.0	
5-1	Coke kiln	72000 lb/h (1)	137,000	14.0	9.8	363.	28.0	7.2	503.2	48.7	Shell
5-2	Coke kiln	72000 lb/h (1)	128,000	14.0	9.8	310	17.8	5.4	421.4	31.0	LA APCD
6	Steel Open Hearth	136,600 lb/heat	15,046	12.0	9.0	321.	34.4	9.7	427.9	57.7	Shell
7-1	FCC/CO boiler (3)	51000 Bpd (1)	110,200 (4)	1.5	12.5 (4)	18. (2)	1.0	5.2	2.7	0.2	Shell
7-2	FCC/chem. oxid (3)	51000 Bpd (1)	91,500 (4)	3.0	12.5 (4)	414.	3.6	0.9	461.4	4.2	Shell
8	Gypsum Calcining Kettle	240 t/d	7,794	--	25.	563.	9.0	1.6	520.0	10.5	Shell
9	Glass Furnace	118 t/d	15,054	12.5	15.	0.	0.0	--	0.0	0.0	LA APCD
10-W	FCC/CO boiler (3)	51480 Bpd	108,000 (4)	--	11.4	15.	3.4	20.7	2.33	0.65	Shell
10-E	FCC/CO boiler (3)	51480 Bpd	108,000 (4)	--	11.4	470.	0.0	0.0	512.8	0.0	LA APCD
10-OA	Odor Incin.	Variable	16,157 (4)	--	--	442.	38.0	7.9	482.1	52.1	Shell
10-S	Sulfur Plt. Incinerator	120 t/d	25,177 (4)	--	--	245. (10)	11.0	4.3	40.0	2.3	Shell
11	FCC/CO boiler	35000 Bpd (1)	143,000	--	22.8	7325 (5,10)	16.0	0.2	1862.7	5.1	Shell
12-1	Sulfuric Acid Plant	263 t/d	14,907	9.5	5.0	367.	11.0	2.9	531.8	20.1	Shell
12-2	Sulfuric Acid Plant	194 t/d	18,524	15.0	0.6	314.	3.0	0.9	47.1	0.57	Shell
13	FCC/CO boiler	12900 Bpd (1)	51,441	1.95	9.5	466.	1.0	0.2	87.2	0.24	LA APCD
14	Brake-shoe debonder	617 shoes/hr	755	16.0	4.4 (8)	478.	3.6	0.7	248.3	2.4	Shell
15	Glass Furnace	152 t/d	16,363	12.5	11.0	27.	--	--	0.2	--	Meter only
16-1	Lead Cupola	90 t/d	18,242	19.5	2.4	45.	10.0	18.2	6.8	2.1	LA APCD
16-2	Lead Cupola	50 t/d	18,079	19.5	5.2	202.	2.8	1.4	37.3	0.7	Shell
16-3	Lead Sweat Furnace	--	--	19.5	--	447.	2.9	0.6	84.8	0.7	Shell
					--	0.	--	--	0.0	--	Meter only

TABLE D-II. Continued

Test No.	Device Type	Process Rate	Stack Flow SCFM (wet)	Stack Gas % O ₂ (dry)	Stack Gas % H ₂ O (vol.)	SO ₂ , ppm (wet)	SO ₃ , ppm (wet)	SO ₂ /SO ₃ % (vol.)	Emission Rates		SOx Test Method
									SO ₂ lb/h	SO ₃ lb/h	
17	Sulfur Plt. Tail Gas Unit/Incin.	50 t/d (1)	2,843	12.0	10.7	104 (6)	3	2.8	3.0	0.11	Shell
18	Sulfur Plt. Tail Gas Unit/Incin.	12 t/d	3,721	12.5	4.4	115.	4	3.4	4.3	0.2	Shell
19	Iron Cupola	11 t/h	18,872	13.0	6.2	8.4	3.8	31.1	1.6	0.9	Shell
20	FCC/CO boiler	10,300 Bpd	32,407	1.4	10.9	420 (7)	3.0	0.7	137.5	1.2	Shell
21-1	Sintering Machine	1925 t/d (1)	152,377	18.5	7.8	230.	4.0	1.7	353.3	7.7	Shell
21-2	Sintering Machine	1925 t/d (1)	106,857	19.5	11.1	269	0.0	0.0	290.5	0.0	LA APCD
21-CB	Coke Oven	485 t/d (1)	58,769	18.5	11.9	197.	4.0	2.0	116.9	4.7	Shell
21-3	Steel Open Hearth	500,000 lb/heat	40,561	12.5	11.0	203.	4.7	2.3	83.3	2.4	Shell
21-4	Blast Furn.	1800 t/d	Not meas.	10.0	13.0	54.	3.0	5.5	--	--	Shell
22-1	FCC/CO boiler	(9)	136,490	2.3	15.9	206	7.0	3.3	284.0	12.1	Shell
22-2	Sulfur Plant Tail-gas Unit	(9)	9,912	0.5	6.7	6.	2.3	29.1	0.6	0.3	Shell
23-1	Well-head Vapor Reactor	4.5 MMB/h	43,466	19.5	4.5	163.	3.0	1.8	71.6	1.7	LA APCD
23-2	Well-head Vapor Reactor	3.12 MMB/h	43,442	19.4	5.1	175.	3.0	1.7	76.9	1.7	Shell
24	Cement Kiln	44 t/h	180,252	--	9.7	6.	0.9	12.5	11.5	2.1	Shell

5802-432

- (8) Estimated based on process calculations.
 (9) Designated as Trade Secret by operator.
 (10) Dry analysis result.

- (1) Design capacity.
 (2) Average value for 8 hr heat.
 (3) Measurements made on two stacks from same FCC unit.
 (4) Values provided by refinery.
 (5) Currently operating on variance. Emissions beyond 1975 will be based on tail gas unit control.
 (6) Steady-state value measured after tightening leaking by-pass valve. Prior to valve adjustment readings up to 1800 ppm were observed.
 (7) Steady-state meter reading after adjustment of H₂S/SO₂ ratio from 0.89 to 2.0. Prior to adjustment readings up to 1200 ppm were observed.

REFERENCES

30. "Determination of Sulfur Trioxide and Sulfur Dioxide in Stack Gases, Absorption - Titration Method," Shell Method Series 62/69, Shell Standardization Committee (North America), 1969.
31. Devorkin, H., et al. "Air Pollution Source Testing Manual," Air Pollution Control District, Los Angeles County, California, Dec. 1972.
43. Urone, P. F., "Source and Ambient Air Analysis for Sulfur Trioxide and Sulfuric Acid: A State-of-the-Art Report," Report prepared for The Intersociety Committee, Vol. II, No. 3, H.L.S., July 1974.
44. Morrow, N. L., Brief, R. S., and Bartrand, R. R., "Sampling and Analyzing Air Pollution Sources," Chemical Engineering, Jan. 24, 1972, p. 85.
45. "Standards of Performance for New Stationary Sources," Federal Register, 36, Dec. 23, 1971.
46. Bloomfield, B., Air Pollution, Vol. II, 2nd Ed., A. C. Stern, ed., Chap. 28, Academic Press, New York, 1968.
47. "Atmospheric Emissions from Sulfuric Acid Manufacturing Process," U.S. Public Health Service Publication No. 999-AP-13, 1965.
48. Hamil, Henry F., "Laboratory and Field Evaluations of EPA Methods 2, 6, and 7," EPA 68-02-0626, October 1973.
49. Hamil, H. F., et al., "Collaboration Study of Method for the Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources," EPA-650/4-75-003, November 1974.
50. Wastlin, Peter R., EPA, Emission Measurement Branch, personal letter, Sept. 27, 1975.
51. Hamil, Henry F., et al., "The Collaborative Study of EPA Methods, 5, 6, and 7 in Fossil Fuel-Fired Steam Generation," EPA-650/4-74-013 NTIS PB 237 695, May 1974.
52. Shigehara, R. T., EPA, Telephone conversation Jan. 20, 1975.
53. Devorkin, H., LA APCD, personal conversation, Jan. 27, 1975.
54. Lisle, E. S. and Sensenbaugh, J. D., "The Determination of Sulfur Trioxide and Acid Dew Point in Flue Gases," Combustion, 36, 12-16.

Blank Page

SOUTH COAST AIR BASIN SO_x INVENTORY

FORM I PRELIMINARY DATA

OWNER/OPERATOR _____

PLANT MAILING ADDRESS _____ ZIP _____

PLANT STREET ADDRESS _____

PLANT CONTACT _____ PHONE () - _____

A. Device Type					
B. Plant Unit Number					
C. Primary Material					
D. Design Rated Capacity					
E. Units of Rated Capacity					
F. Is Exhaust SO ₂ Removed by an SO ₂ Control Device?					
G. Estimated SO ₂ Emission at Design Capacity, lb SO ₂ /hr, (after control unit)					

Please complete and return this preliminary form as soon as possible prior to completion of the remaining questionnaire pages.

5802-432

APPENDIX E

POINT SOURCE OPERATIONAL DATA QUESTIONNAIRES

The forms contained in this appendix were transmitted to 39 plants in the South Coast Air Basin that process materials from which SOx emissions can occur. The data collected was used to revise preliminary inventory operations assumptions to reflect more realistic operation in final SOx inventory emission rates. Much of the data provided was designated as trade secret so the completed forms are not included in this report. Access to these data is permitted only to those directly involved in the inventory program.

SOUTH COAST AIR BASIN SO_x EMISSION INVENTORYFORM II DEVICE RATING AND OPERATION DATA

(Devices operating before Jan. 1, 1975)

OWNER/OPERATOR _____

PLANT MAILING ADDRESS _____ ZIP _____

PLANT STREET ADDRESS _____

PLANT CONTACT PERSON _____ PHONE () - _____

A. Device Type						
B. Plant Unit Number						
C. APCD Applic/Permit No.						
D. Primary Input Material Type						
E. Primary Output Product Type						
F. Design Rated Capacity						
G. Units of Design Rated Capacity						
H. Rating Based on Input or Output?						
I. Process Batch or Continuous?						
J. Batch Process, Minutes or hours/batch	Average Annual 1974					
K. Daily Operation, Hours/day	Aug. 1974					
L.	Dec. 1974					
M. Weekly Operation, Days/Week	Aug. 1974					
N.	Dec. 1974					
O. Annual Operation, Hours/Year	1972-Hrs.					
P.	1973-Hrs.					
Q.	1974-Hrs.					

5802-432

SOUTH COAST AIR BASIN SO_x INVENTORY

FORM III MATERIAL USE AND PRODUCT OUTPUT

OWNER/OPERATOR _____

		Plant Total	Plant Unit Number				
A. Input Material Use	Type						
B.	Units						
C.	Aug 1974						
D.	Dec 1974						
E.	Annual 74						
F. Input Material Average Sulfur Content	Units						
G.	1974						
H. Product Output	Type						
I.	Units						
J.	Aug 1974						
K.	Dec 1974						
L.	Annual 74						
M. Product Average Sulfur Content	Units						
N.	1974						

5802-432

SOUTH COAST AIR BASIN SOX INVENTORY
FORM IV PLANT UNIT EXHAUST, CONTROL UNITS, AND STACK DATA

OWNER/OPERATOR _____

Plant Unit Exhaust (Before Control Unit)		Plant Unit Number				
A. Rated Exhaust Flow, SCFM						
B. Average O ₂ Content, % Vol.						
C. Average SO ₂ Content, % Vol or ppmV						
D. Plant Unit	Aug 74 - Tons/day					
E. Exhaust SO ₂	Dec 74 - Tons/day					
F. (Before control Unit)	1974 - Tons/year					

Emission Control Units

G. Emission Control Unit I.D. Number					
H. Equipment Type					
I. Process Name					
J. APCD Applic/Permit No.					
K. Date Placed in Operation					
L. Design Control Efficiency, % Weight SO ₂ Removed					

Stack Data

M. Number of Exhaust Stacks					
N. Rated Stack Flow, SCFM					
O. Stack Height, feet					
P. Average O ₂ Content, % by Vol.					
Q. Average SO ₂ Content, % Vol. or ppmV					
R. Average % of SOx as SO ₃ or H ₂ SO ₄					
S. SO ₂ Emitted	Aug 74 - Tons/day				
T.	Dec 74 - Tons/day				
U.	1974 - Tons/year				

5802-432

SOUTH COAST AIR BASIN SOx INVENTORY
FORM V PROJECTED OPERATIONS AND NEW UNITS

OWNER/OPERATOR _____

Plant Units In Operation Before 1/1/75		Plant Total	Plant Unit Number				
A. Input Material Use	Type						
	Units						
	1975						
	1976						
	1980						
F. Product Output	Type						
	Units						
	1975						
	1976						
	1980						

New Plant and Control Units: In Operation 1/1/75 - 12/31/80

- K. If NO new plant units or new SOx control units for existing plant units are anticipated, check here _____.
- L. If new plant units or new SOx control units are to be placed in operation, list units below and you will be contacted if further information is required.

5802-432

APPENDIX F

FUEL DESULFURIZATION

TABLE OF CONTENTS

	<u>Page</u>
F-1.0 INTRODUCTION	F-1
F-2.0 CRUDE PROPERTIES	F-3
F-3.0 DESULFURIZATION PROCESSES	F-9
F-4.0 DESULFURIZATION COSTS	F-15
REFERENCES	F-28

Blank Page

APPENDIX F

FUEL DESULFURIZATION

F-1.0 INTRODUCTION

The use of low sulfur fuel oil has been the major technique for SOx emissions control in the basin. Since about 1967 all counties in the basin have restricted liquid fuel sulfur content to less than 0.5% S. Prior to that year fuel at about 2.0% S was burned in utility boilers and implementation of the regulation resulted in a more than 135 tons/day reduction of utility SOx emissions in Los Angeles County alone.

The increased use of natural gas, starting in the basin about 1958, was also effective in limiting SOx emissions. However, about 1968, gas use reached a maximum and in following years increased curtailment of natural gas forced the burning of additional low sulfur fuel oil by both in utility boilers and other devices capable of burning oil. In 1973 this trend was sharply accelerated and projections indicate that SOx emission rates, even with low sulfur fuel use, will rapidly increase to levels equivalent to prior years when high sulfur fuels were burned.

As fuel sulfur limitation has clearly been established as a prime SOx control technique this report section discusses the technology of fuel desulfurization and the problems and costs that would result from reduction of fuel sulfur contents to levels below the current regulation.

Natural gas is accepted as a clean sulfur-free fuel. It should be recognized, however, that this gas is not naturally sulfur-free. Natural gas desulfurization can, if uncontrolled, result in substantial SOx emissions. Claus plants at the Lacq field in France were estimated to yield 10% of the total sulfur oxides emissions for that nation in 1970 (Ref. 55). Gas from the Panther River field, Alberta, Canada, contains 86% hydrogen sulfide (H_2S) (Ref. 56) and desulfurization of this gas is a major source of sulfur in the world market (Ref. 57).





Development of natural gas fields that lie in the Outer Continental Shelf off the coast of Southern California is projected to provide one of the major sources of natural gas to replace curtailed supplies. The gas from these fields is anticipated to contain only 1.0 to 1.5% H_2S and Claus plant facilities to remove this sulfur will be located off shore (Ref. 58). While sulfur content is low, the quantities involved could result in significant SO_x emissions reaching the basin in the absence of adequate controls. Claus plant tail gas clean-up processes, as discussed in Appendix I, are available that can reduce SO_x emissions to a negligible amount. As use of these processes is most likely planned for the off shore facilities there should be no significant impact on air quality in the South Coast Air Basin.

F-2.0 CRUDE PROPERTIES

The ability to provide low sulfur fuels is dependent primarily on the ability to obtain crude petroleum stocks. The yield of low sulfur fuel oil is also dependent on the properties of the crude as relate to distribution of the sulfur within the crude fractions and this in turn influences the processes used and costs for desulfurization.

The amount of sulfur that any particular crude contains will vary widely depending upon its geological history. The maximum sulfur content of a crude that has been measured is 13.95% from a seepage in Utah (Ref. 56). Crudes having less than 0.1% S are not unusual but 1-5 percent sulfur appears to be a more normal level. Sulfur compounds tend to accumulate in the higher boiling fractions as multiring thiophenes and cyclic sulfides. Aliphatic sulfur compounds are predominant only in the very low boiling range of the crude oil. Weight percent sulfur as a function of volume percent distilled for the Gach Saran, Iran, crude, is shown in Figure F-1 (Ref. 59) indicating highest sulfur in the heaviest (residual) fractions.

API Research Project 48 (Ref. 56) identified the sulfur compounds present in crude (naptha fraction) according to compound type as shown below:

	Typical structures
Group:	
Hydrogen sulfide.....	H_2S
Mercaptan.....	C_n-SH
Free sulfur.....	S
Disulfides.....	$C_m-S-S-C_n$
Sulfides I.....	C_m-S-C_n ,  , 
Sulfides II.....	 , 
Residual sulfur.....	

5802-432

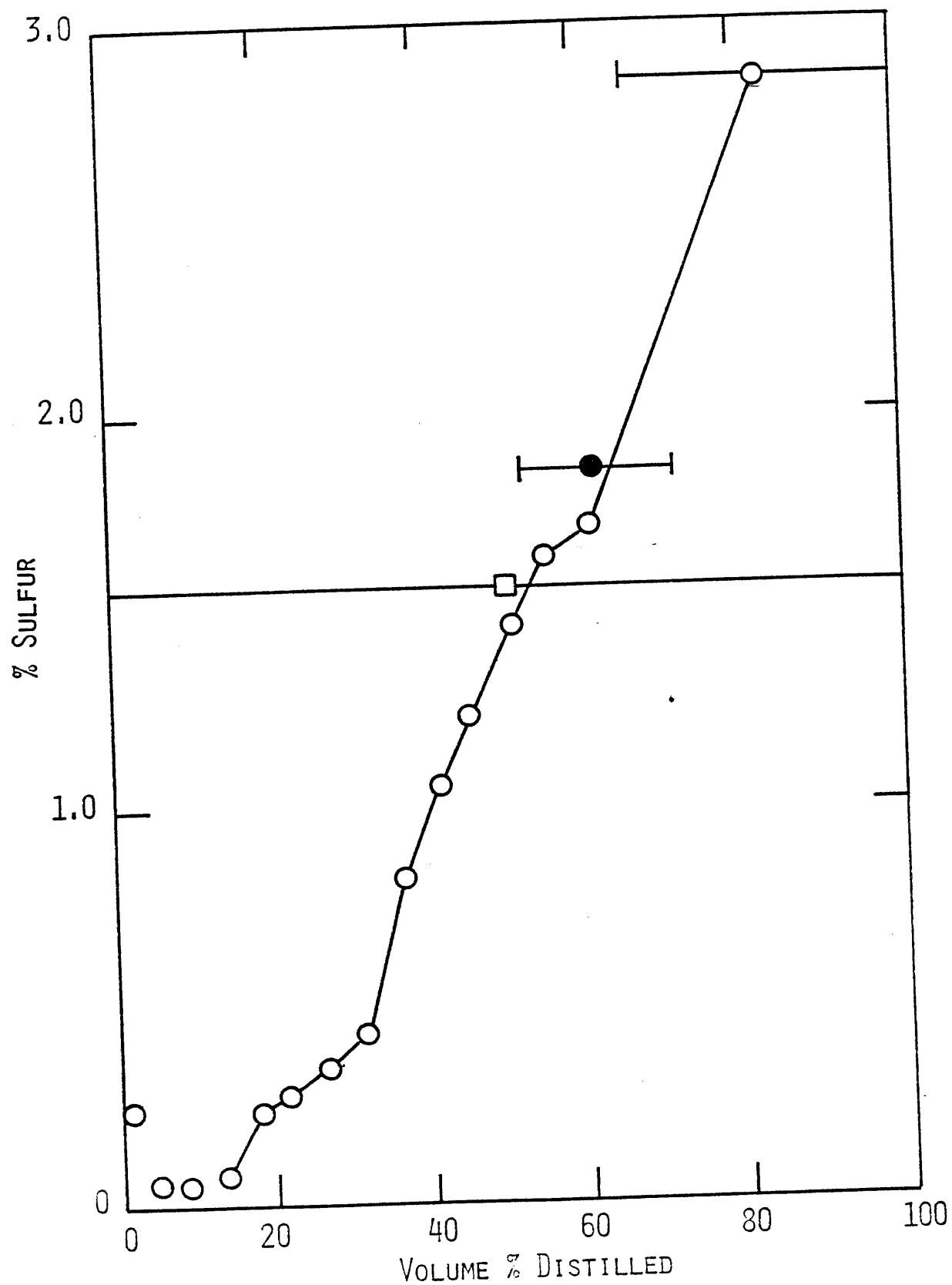


FIGURE F-1. DISTRIBUTION OF SULFUR IN WHOLE CRUDE - GACH SARAN, IRAN CRUDE.

The residual sulfur included those higher molecular weight members or types which because of their complex chemical structure or for other reasons, could not be classified.

Since that time, the comparisons of the 700-1000°F cut from five crudes (Gach Saran, Iran; Swan Hills, Canada; Reduse, Wyoming; Wilmington, California; Prudhoe Bay, Alaska) have been investigated in detail (Ref. 60). The percent sulfur in the total Gach Saran crude was 1.57% and the sulfur within the 700-1000°F cut was 1.85%. The distribution of sulfur by chemical group within the 700-1000°F cut is shown in Figure F-2. All significant amounts of sulfur were contained within the mono-aromatic, diaromatic and polyaromatic fractions which together represent about 50 percent of the 700-1000°F cut. The sulfur content within each fraction increased with increasing aromaticity up to a maximum of 5.9% sulfur in the polyaromatic fraction (asphaltenes). Thus the major portion of the sulfur is situated in the more complex molecules that are harder to desulfurize.

Sulfur containing compounds are identified by chemical type in Figure F-3 for the five crudes investigated. Molecular weights of these compounds ranged between 250-600 with an average of about 400. Of the sulfur compounds present in crude oils, mercaptans are the least stable, followed by sulfides and then thiophenes which are the most stable. Higher molecular weight and branch chained species are less stable than their lower molecular weight and straight chain homologs.

The basic desulfurization process involves the addition of hydrogen which replaces the sulfur atoms in the hydrocarbon molecules. The hydrogen also bonds with some carbon in molecules that have double or triple carbon bonds. As most sulfur is located in the multi-bonded compounds, and these compounds are in turn concentrated in the heavier end of the crude, greater amounts of hydrogen are required to desulfurize residual fuels. As a result, the costs to desulfurize residual fuels as compared to distillates can be expected to be higher.

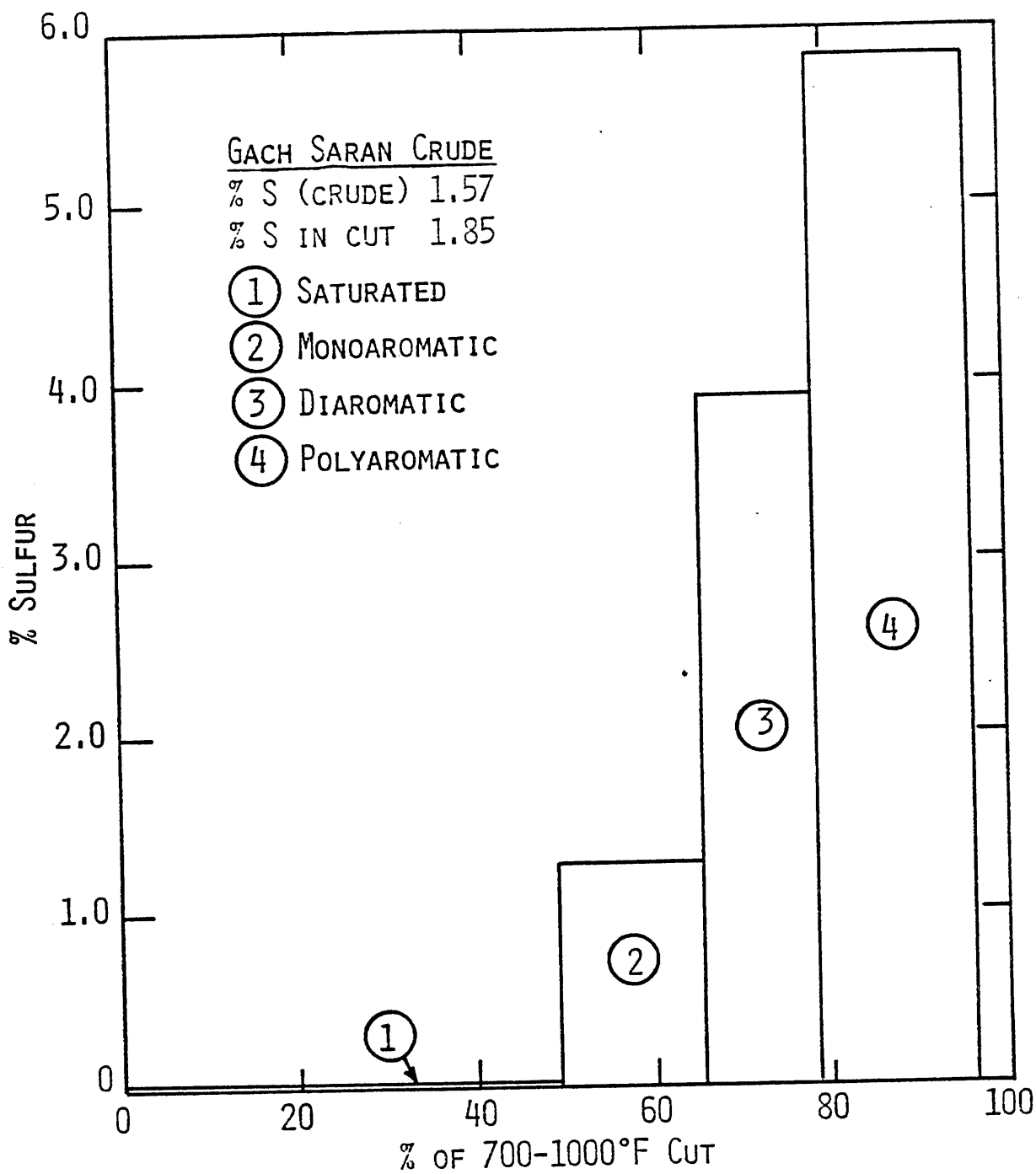


FIGURE F-2. DISTRIBUTION IN 700-1000°F CUT ACCORDING TO CHEMICAL ANALYSIS FRACTION.

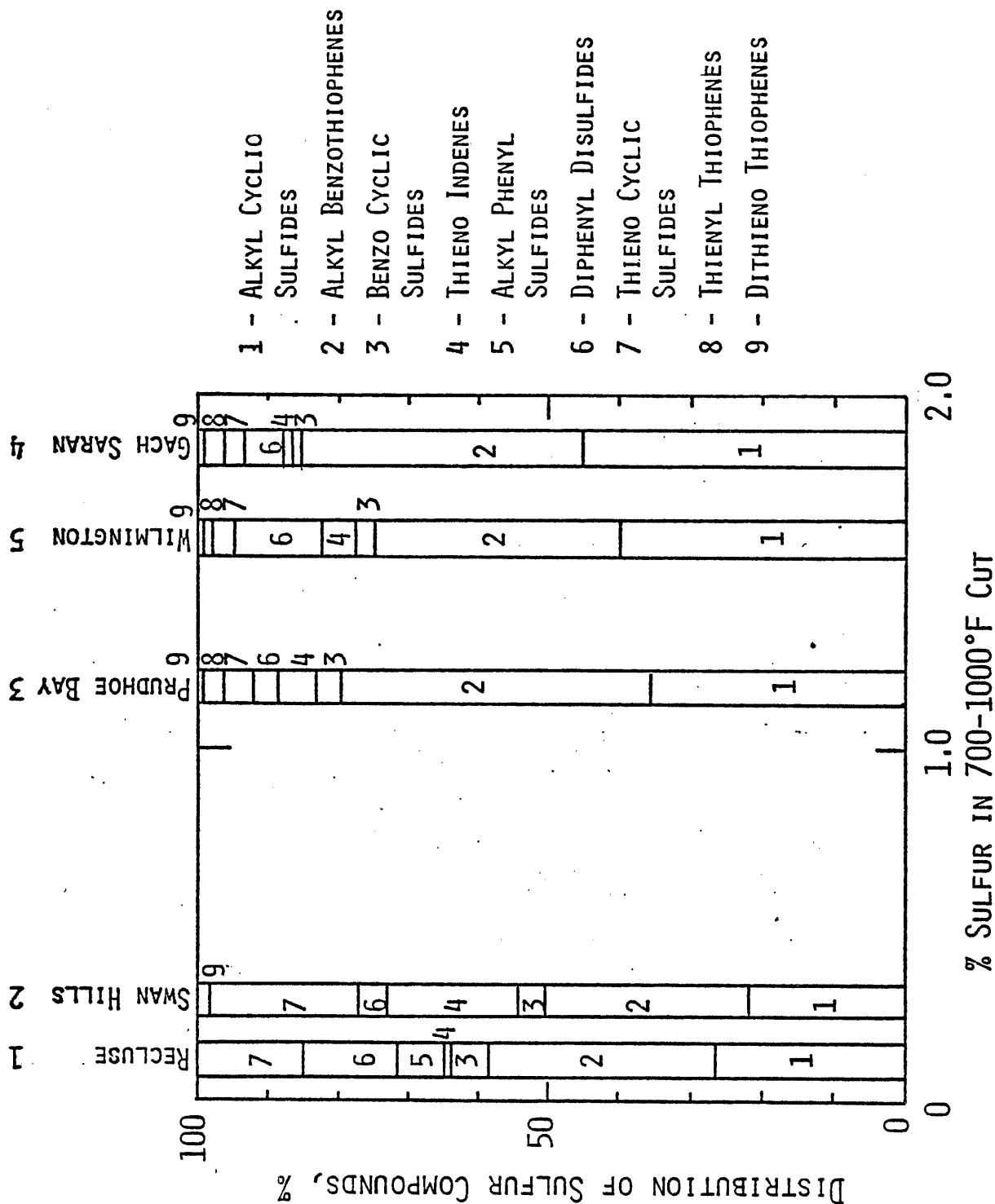


FIGURE F-3. COMPARISON OF SULFUR COMPOUND DISTRIBUTION IN 700-1000°F CUT.

A further difficulty is that metallic compounds are also concentrated in the heavier ends and these tend to deactivate the catalysts that are used to accelerate the hydrogenation process. This results in increased catalyst costs for residual oil desulfurization.

F-3.0 DESULFURIZATION PROCESSES

Any future consideration that is given to reduction of fuel sulfur content below the current 0.5% S level, must include the consideration of processes available and the technical feasibility of producing large quantities of low sulfur distillate and residual fuels. Hydrodesulfurization of distillate fuels has been performed for many years and this section will concentrate primarily on the process changes required to obtain reduced sulfur residual fuels.

The large variety of target sulfur levels, product distribution, and the effects of specific crude oil properties has resulted in the proliferation of processing routes available for conversion of crude into low sulfur residual fuel oil. It helps to divide these routes into two categories, direct and indirect. Direct desulfurization routes process a whole residuum and must reckon with the problems arising from organometallic feed constituents. Since the whole residuum is processed, low sulfur levels may be attained in the final product.

Indirect desulfurization routes employ a separation process, such as vacuum distillation, solvent deasphalting, or visbreaking, to recover low metal-content oils. These oils are hydrodesulfurized using straightforward process techniques and improved catalysts. The desulfurized product is then blended back with the remainder of the residuum to achieve an intermediate degree of desulfurization. The choice of desulfurization process route depends to a large extent on the characteristics of the available residuum and the desired sulfur level of the fuel oil pool. Feed characteristics of particular importance are sulfur, metals, and asphaltene content.

The indirect process has been the most prevalent approach as it is less costly but because of the blending required the sulfur levels obtainable are higher than for the more costly direct process. Some of the newer processes are basically an indirect method, in that two streams are processed, but both streams are desulfurized leading to a more optimum process with low sulfur contents similar to those obtainable with the direct processes.

The most important factor in developing commercially viable residual fuel desulfurization processes has been the development of catalysts having greater activity and longer process life. Catalyst deactivation occurs by at least two separate mechanisms -- the laydown of coke and the laydown of feed metals. The former deactivation is depressed by higher pressures, but the latter is not. Lower pressure operation results in lower hydrogen consumptions but higher catalyst consumptions. The optimum pressure varies with feed source and product sulfur level.

With high metals feeds, considerable attention needs to be paid to the demetalation kinetics - in terms of both the product fuel oil metal content and also in terms of catalyst life. Most of the feed metals react at desulfurization conditions to form metal sulfides. If these reaction products deposit in the interstices of the catalyst bed, then serious bed pressure drop increases can occur. If the reaction occurs inside the pores of the catalyst, then the sulfide deposit will ultimately deactivate the catalyst.

The hydrocracking of residuum is nearly 10 times more difficult than gas oil hydrocracking. This is attributed to the large asphaltenic molecules present and high metals content in the residua. In spite of these increased difficulties commercial processes have been developed for effective desulfurization of residual oils down to levels as low as 0.1% sulfur. Some of these processes are discussed below.

Eleven desulfurization units are operating worldwide with a total capacity of 325,000 BBL/d, with the bulk of the facilities (six units with 235,000 BBL/d capacity) in Japan (Refs. 61, 62, 63). Japanese units range in size from 28 to 45 thousand barrels per day. From the start-up of the pioneer HDS unit in 1970 to the most recent in 1974, none has failed to meet design performance. A 50,000 barrel per day unit capable of producing 0.1 percent sulfur product will be started in Japan later this year.

Gulf Research and Development has recently described their process (Refs. 61, 62) for hydrodesulfurization of residual fuels. The process is available in three versions of increasing sulfur removal, designated Types II, III and IV, producing 1.0, 0.3, and 0.1% S fuel oil, respectively. Figure F-4 shows a flow sheet for the Gulf HDS Type II process consisting of a single stage. Two stages are used for the Type III process and the Type IV process employs three stages and two different catalysts. Cost for the Gulf processes have been presented (Ref. 61) for processing Kuwait and Alaskan North Slope atmospheric tower bottoms (see Section F-5). The processes have been demonstrated in the laboratory but no full scale plants have apparently been built.

A somewhat different scheme has been developed by IFP (Institute Francais du Pictrole) (Ref. 65). Figure F-5 illustrates this process. Atmospheric resid is first fractionated in a vacuum still. The vacuum gas oil distillate is fed directly to a VGO hydrodesulfurization unit. Vacuum bottoms are deasphalted to give a heavy de-asphalted oil low in metals and asphaltenes, and residual asphalt. DAO is desulfurized in a separate HDS unit. IPF has chosen this process over two other options, one of which is direct hydrodesulfurization of the atmospheric bottoms. The first commercial plant has been on stream since 1966. The total capacity now under license is about 150,000 barrels per stream day (BPSD). The process is reported to produce 0.3% S oil from 3.0%S crude at a cost of about \$0.90/BBL.

A third approach is that exemplified by the vacuum residuum desulfurization unit (VRDS) now being installed by Chevron at El Segundo, California (Refs. 66, 67). This is illustrated in Figure F-6 and is called the VGO/VRDS route. The atmospheric bottoms are sent to a vacuum tower where the tops and bottoms are individually hydrodesulfurized. According to Chevron, the technical advantages of the VGO/VRDS scheme over single-stream direct processes arise because all of the heavy asphaltenes present in the crude oil are found in the 1000°F+ vacuum

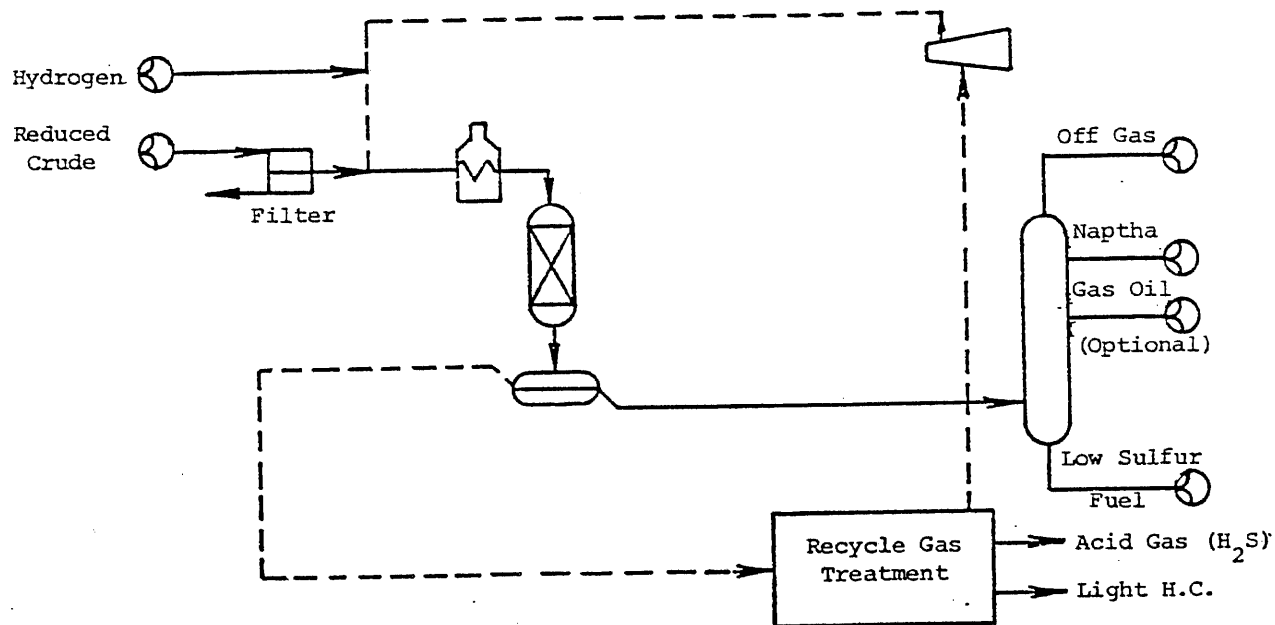


FIGURE F-4. FLOWSHEET, GULF HDS TYPE II PROCESS.

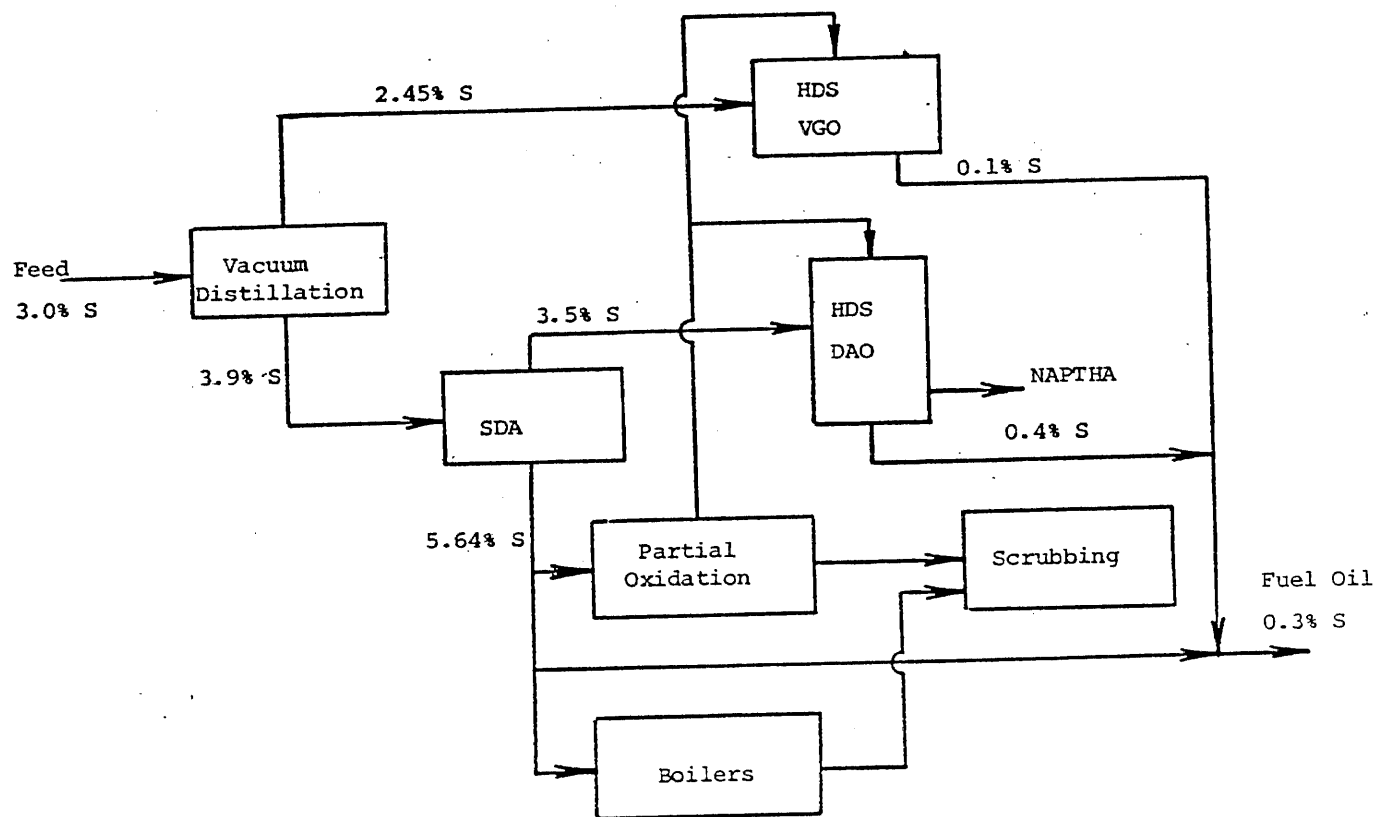


FIGURE F-5. SCHEMATIC OF IFP PROCESS.

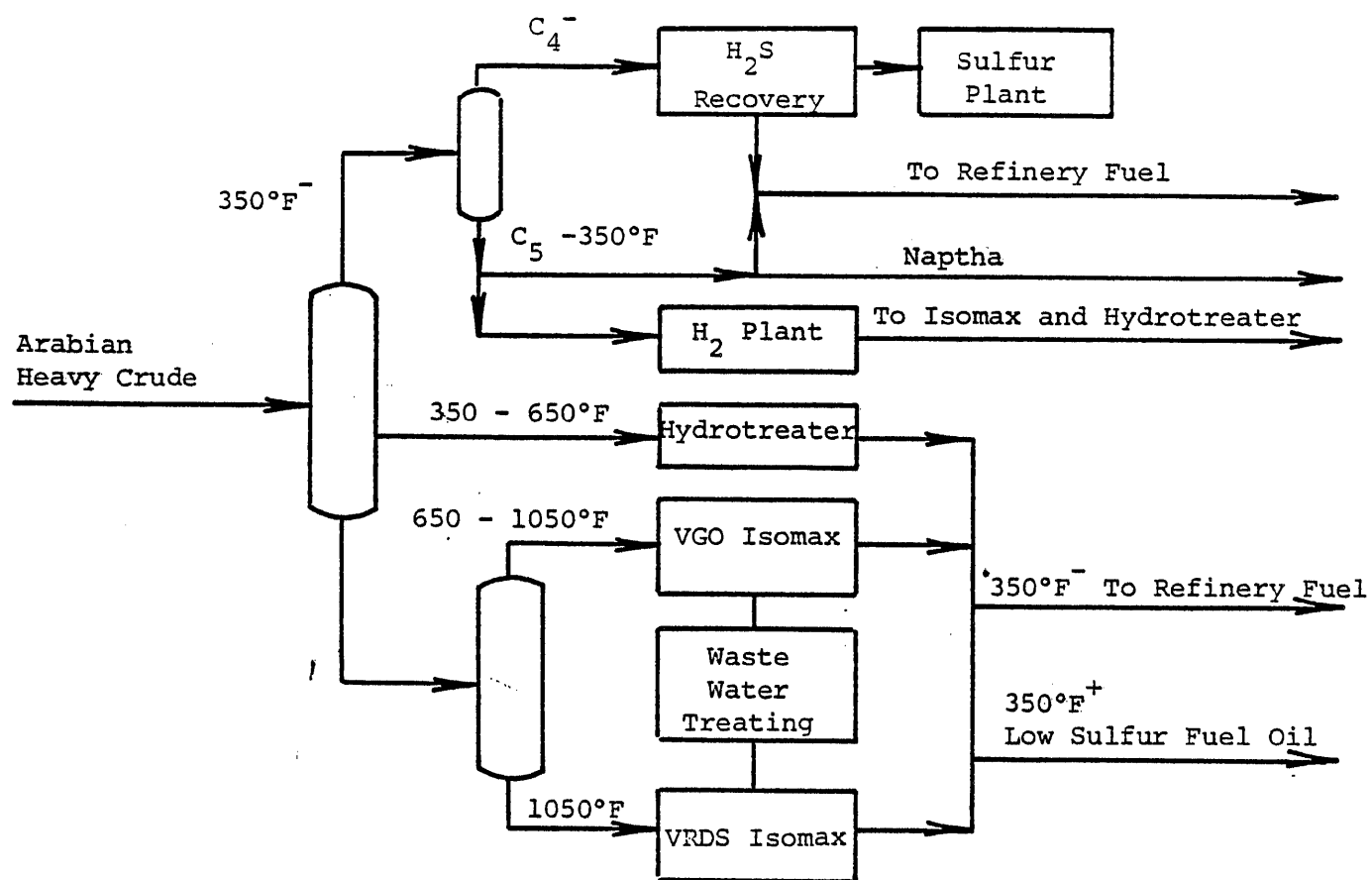


FIGURE F-6. VGO-VDRS PROCESS.

residuum. These asphaltenes contain the most refractory sulfur-containing molecules and also all of the metal contaminants present in the crude. These are the feed components which contribute the most to catalyst deactivation in residuum processing. Significant savings in hydrogen consumption are also realized if the vacuum gas oil and the vacuum residuum are processed separately at their optimum conditions. This process is being installed to provide over 100,000 BPD of low sulfur fuel oil at less than 0.5% sulfur primarily to Southern California Edison power plants. Additional sulfur extraction and handling capacity would undoubtedly be required to provide oils at significantly less than 0.5% S.

The foregoing processes have demonstrated the technology is available to obtain low sulfur fuels in the range of 0.1 to 0.5% S. Total refining capacity for providing these lower sulfur levels to basin users is not specifically known but is undoubtedly well below the projected fuel consumption rates that will occur in the basin in future years.

F-4.0 DESULFURIZATION COSTS

To determine the most cost effective method of reducing sulfur oxide emissions from oil burning combustion sources, it is necessary to compare the future costs of low sulfur fuel oils to the projected costs of other potential reduction methods. Prices of low sulfur fuel oils have been so unstable during the past several years, however, that it is probably not feasible to use the market prices as indicators of what these fuels might cost in the future. The objectives of this section will be to present the results of an "actual cost of manufacturing" analysis by which it may be possible to make reasonable predictions of future low sulfur fuel oil prices.

In 1973, actual prices of low sulfur fuel oil were: Gulf Coast, \$4.15 (0.6% S), Mid-Continent (1% S), \$2.60, and for No. 5 fuel oil (1% S), \$5.04 in Chicago, and \$4.59 in New York. At that time, refineries, apparently were selling fuel oil at a loss as the cost of manufacturing (cost of crude plus operating costs) was about \$4.82/BBL (Ref. 68). In May 1974, the cost of manufacture was about \$9.36/BBL when the prices were: Gulf Coast \$4.95, Mid-Continent, \$7.00, No. 5 (1% S), \$13.44 at Chicago and \$12.29 at New York. Because the price and availability of low sulfur fuel oil are of such central importance to the energy and environmental problems of the Basin and because of the uncertainty associated with both, some discussion of the factors involved in determining refinery product prices is included below.

Selling prices in a joint-product industry (such as petroleum refining) do not equal the cost of manufacture except by coincidence. This discrepancy is at the heart of the confusion about prices and costs. Prices of straight-run products (May 1973) in the Mid-Continent U.S.A.

were about:	<u>\$/BBL</u>
Gases (FOE)	1.16
Naptha	4.20
Kerosine	5.00
Diesel fuel	4.80
No. 2 dist.	4.62
Residue	2.80

Yet, the cost of producing each of these products by crude distillation was substantially the same (about \$3.86-3.93/BBL) (Ref. 69).

Many factors in the market, along with competition between refiners, here and abroad, has led to a market structure that is not directly related to the cost of manufacture of each product. The total income from all products, however, must be equal to the total manufacturing costs plus profit. Not surprisingly, then, gasoline (a dominant product) manufacturing costs have been and are reasonably close to market prices. This is because refineries and economists have often adopted gasoline prices that would make the refinery income balance with the expenses (Ref. 70). For \$8.90/BBL crude oil in 1974, the calculated price of gasoline (manufacturing cost and profit) was 26.2¢/gal. The actual average market price for 1974 was 26.6¢/gal.

It has not been possible to make similar statements regarding fuel oils in the past, as low sulfur fuel oils have been a relatively minor refinery product. Their market price has not necessarily reflected their cost of manufacture. Rather, it has reflected what they could bring in market place. The contention here, however, (Ref. 69) is that as the projected demands and production capacity for low sulfur oils increases, the market price (cost of manufacturing plus profit) of low sulfur fuel oils may come more into line with their actual costs of manufacturing. Therefore, if the actual costs of manufacturing can be developed and projected to a future date, future costs of low sulfur fuel oil can also be predicted has a function of crude oil prices.

In the past, manufacturing costs (cost of crude plus operating costs) were governed by operating costs because crude oil prices changed slowly. Now the situation is reversed so that the cost of the crude comprises 75 or even 95% of the manufacturing cost (Ref. 71). Operating cost is still important as it is about the only cost item that can be controlled. But the price of crude oil is the dominant factor. With this in mind, Nelson has projected refinery product manufacturing costs to 1978.

The costs associated with individual refinery operations are generally not available. However, Nelson previously published a compilation of articles (Guide to Refinery Operating Costs) (Ref. 74) from which refinery costs can be derived. These costs can be advanced to the desired time period by means of the Nelson refinery operating cost index published monthly in the Oil and Gas Journal. Of particular interest is the series of articles (Refs. 68-73) published this year (1975) which deal with the manufacturing cost of refinery products since May of 1973 and which are projected to 1978.

In forecasting the cost of petroleum products for the years 1975-1978, Nelson used the year 1973 as a basis, as it was the last somewhat normal year. Costs of various refinery operations and processes were determined as a function of refinery complexity and were brought forward to May 1973, by means of the Nelson refinery operating index.

An indication of what the refinery operating costs were in 1973 is shown in Table F-I. Projected refinery operating costs relative to 1973 are shown in Figure F-7 and F-8 as a function of crude price (Refs. 71,73). These figures show recent sharp increases as the result of inflation and increased refinery fuel costs.

From Table F-I, the 1973 average operating cost for desulfurizing topped crude is about \$1.29/BBL. Using Figure F-7, this leads to operating costs of \$2.11 and \$2.27/BBL for \$8 and \$12 crude in 1975 (\$10.11 and \$14.27, respectively for manufacturing costs). For 1978, the operating costs are \$2.60 and \$2.68/BBL with manufacturing costs of \$10.60 and \$14.68/BBL. Similar manufacturing costs for low sulfur residual fuels can be obtained directly using Figure F-8.

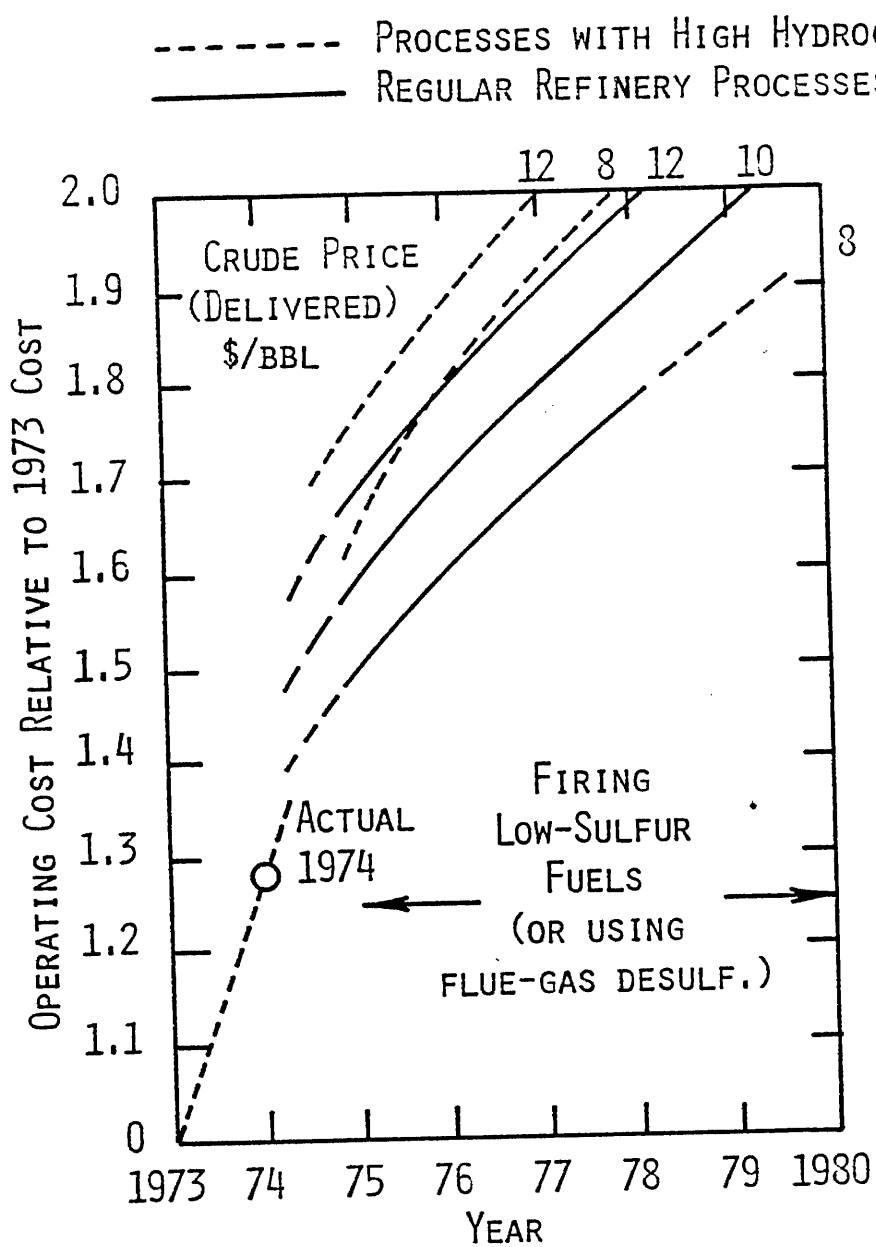
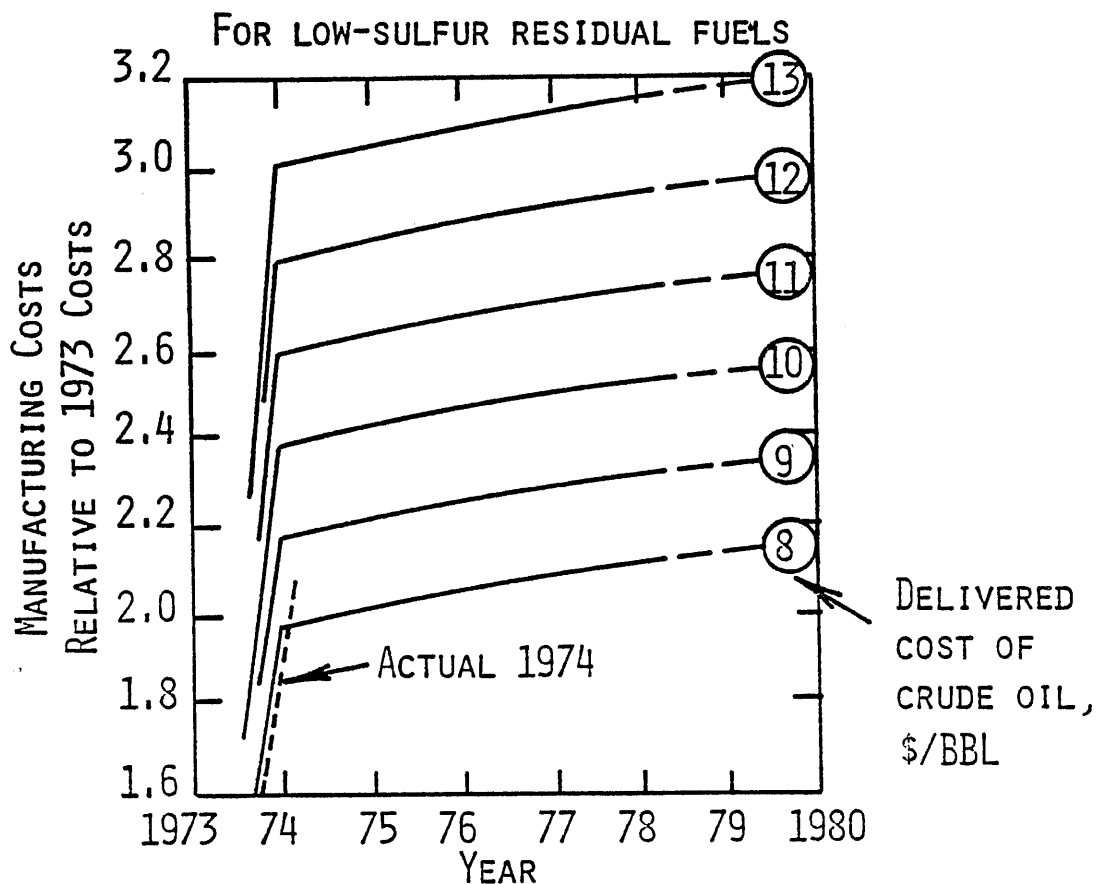


FIGURE F-7. PETROLEUM OPERATING COST INDEX
 RELATIVE TO 1973.

TABLE F-I

1973 U. S. REFINERY OPERATING COSTS FOR DESULFURIZATION

<u>Sulfur Reduction</u>	<u>Feed To Process</u>	<u>Operating Cost \$/BBL From</u>	
		<u>Feed</u>	<u>Crude</u>
2.6-.2	Gas Oil	0.75	0.92
3.5-.3	Topped Crude	1.35	1.52
5.5-.5	"	1.30	1.48
5.5-.8	"	1.24	1.42
3.5-.5	"	1.16	1.33
3.5-.8	"	1.10	1.27
2.0-.5	"	1.02	1.18

FIGURE F-8. PETROLEUM MANUFACTURING COST INDEX
RELATIVE TO 1973.

A recent paper (Ref. 61) has provided information on the total manufacturing cost for desulfurizing atmospheric bottoms (3.8% S) of Kuwait crude for a specific process (Gulf HDS). These costs were based on a crude value of \$9.00 and a first quarter, 1975, basis. The costs are \$1.40 for reduction of sulfur to 1.0%, \$1.98 for reduction to 0.3% and \$2.68 to take the sulfur content of the atmospheric bottoms down to 0.1%. The point was made that substantially higher or lower costs could be involved with different residuals. From Table F-I, the base cost (1973) for desulfurizing topped crude (atmospheric bottoms) containing 3.5% sulfur to 0.3% sulfur, is \$1.35. From Figure F-7, the 1975 operating cost factor for \$9.00 crude is 1.67. Therefore, the manufacturing cost for desulfurization obtained using the general correlation of Nelson is \$2.25. In this case, the agreement of the two estimated manufacturing costs is within 13 percent.

In Figure F-9, the cost of desulfurizing atmospheric bottoms in 1973 is shown for the levels of sulfur in the feed. The data are from Table F-I. Using the 3.5% sulfur level feed as a base, desulfurization costs to 1978 are compared in Figure F-10. The projection is based on Figure F-7. Also shown are desulfurization costs as recently published by Gulf Research (Ref. 61). As a matter of comparison, desulfurization costs are presented by Meredith in 1967 (Ref. 75), and are shown in Figure F-11. This figure indicates that, at the time Rule 62 was implemented to limit liquid fuels to 0.5% S, the cost was between \$0.75 and 1.0 per barrel to obtain 0.5% S fuel from 2.6% S crude. As shown in the preceding figure these costs have considerably increased since that time.

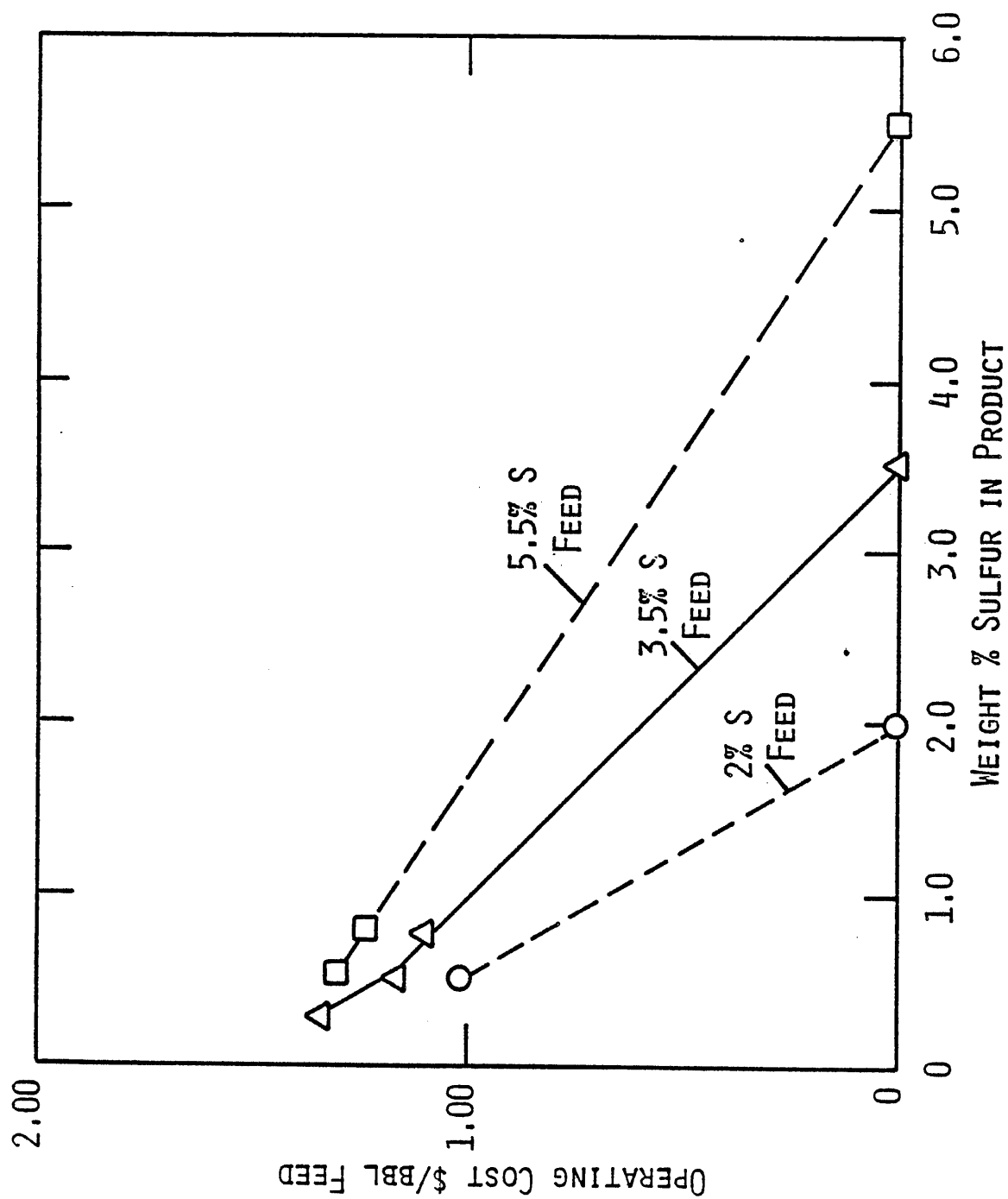


FIGURE F-9. COST OF DESULFURIZING TOPPED CRUDE IN U.S.: 1973.

5802-432

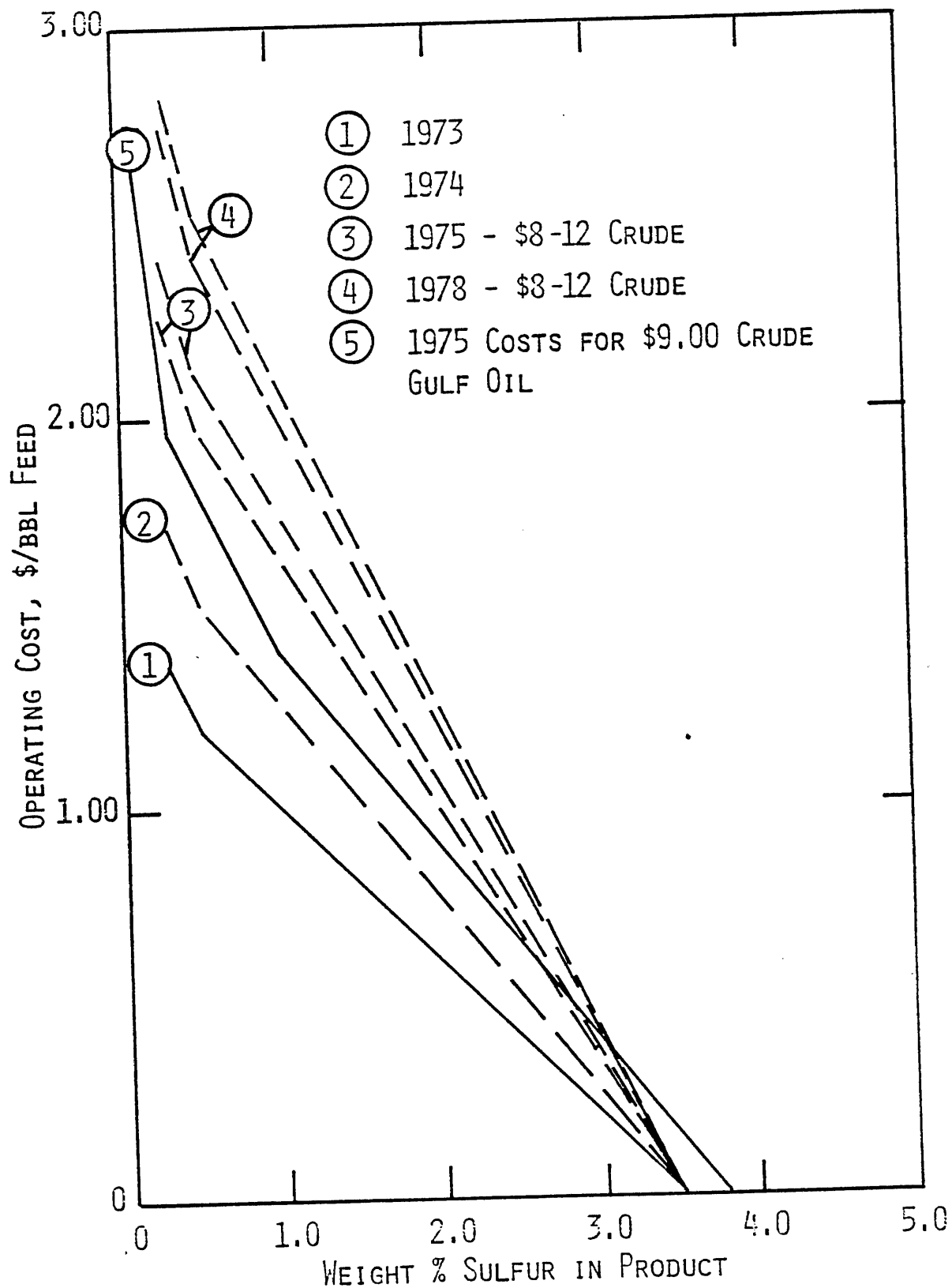


FIGURE F-10. COST OF DESULFURIZING TOPPED CRUDE IN U.S. FOR 1973, 1974, 1975, 1978.

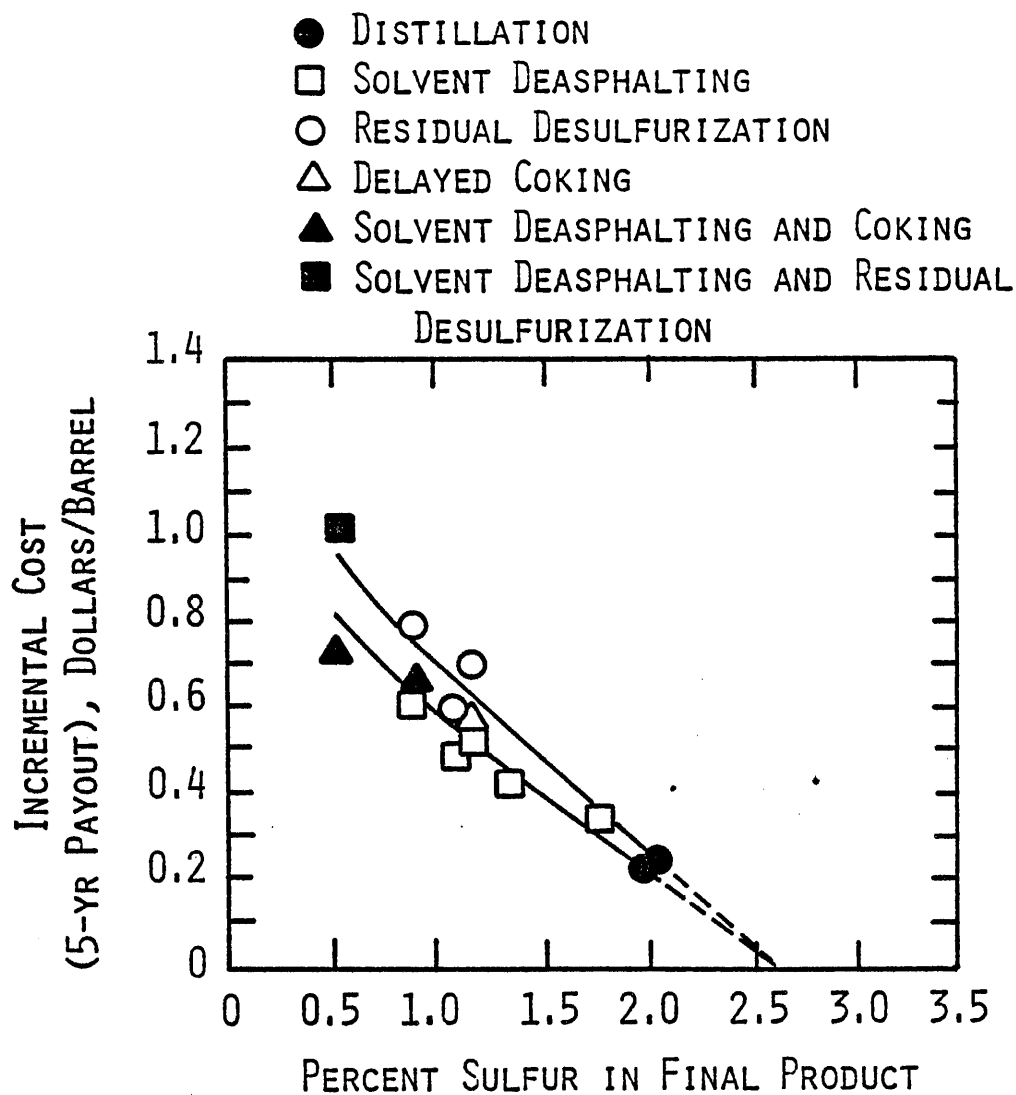


FIGURE F-11. COST OF REMOVING SULFUR FROM FUEL OIL IN 1967.

Operating cost for fuel desulfurization in the low sulfur range is shown in Figure F-12 for 3.5% sulfur feed at the 1975 price level. For 0.5% sulfur product the cost is \$2.11/barrel and incremental costs over this amount for lower levels of product sulfur are also shown in the same figure. Incremental costs over the 0.5% S level are \$0.12, 0.27, 0.57, and 1.11 per barrel for 0.4, 0.3, 0.2, and 0.1% sulfur respectively. These are the specific incremental costs used in reduction potential estimates for this program but the values have a fairly high degree of uncertainty and could vary as much as +100% depending on various factors such as the process used and crude properties.

The cost/benefit ratio used in this program for SO_x reduction is taken as a direct function of desulfurization cost and sulfur content reduction. The cost considered is therefore only based on the increased manufacturing cost of the fuel. This assumes no additional cost differential in marketing or fuel handling at the users facility.

The incremental cost/benefit ratio, for a small reduction in sulfur content relative to any given sulfur content, is indicated on upper curve of Figure F-13. For example, with a fuel initially at 0.2% S, a small reduction in sulfur content would result in a direct SO_x reduction at a cost/benefit ratio of about \$1200/ton. The upper limit criteria defined in this program as \$2000/ton would be reached at the 0.14% sulfur level. This figure shows that reductions in the 0.5 to 1.0% S range have a very attractive incremental C/B ratio at less than \$300/ton. The incremental C/B ratio increases sharply below the 0.5% sulfur level. As noted previously the cost uncertainty is such that the criteria of \$2000/ton could be easily reached at the 0.2% sulfur level.

The lower curve in Figure F-13 shows the overall cost/benefit ratio for reductions from the current basin regulation level of 0.5% sulfur as a function of specified lower sulfur levels. Thus a specified reduction from 0.5% to 0.1% sulfur would result in an overall C/B ratio of \$900/ton. However, as indicated by the upper curve, the incremental reduction from 0.14% to the final 0.1% S would exceed \$2000/ton and thus not be considered cost effective according to the criteria set for this program.

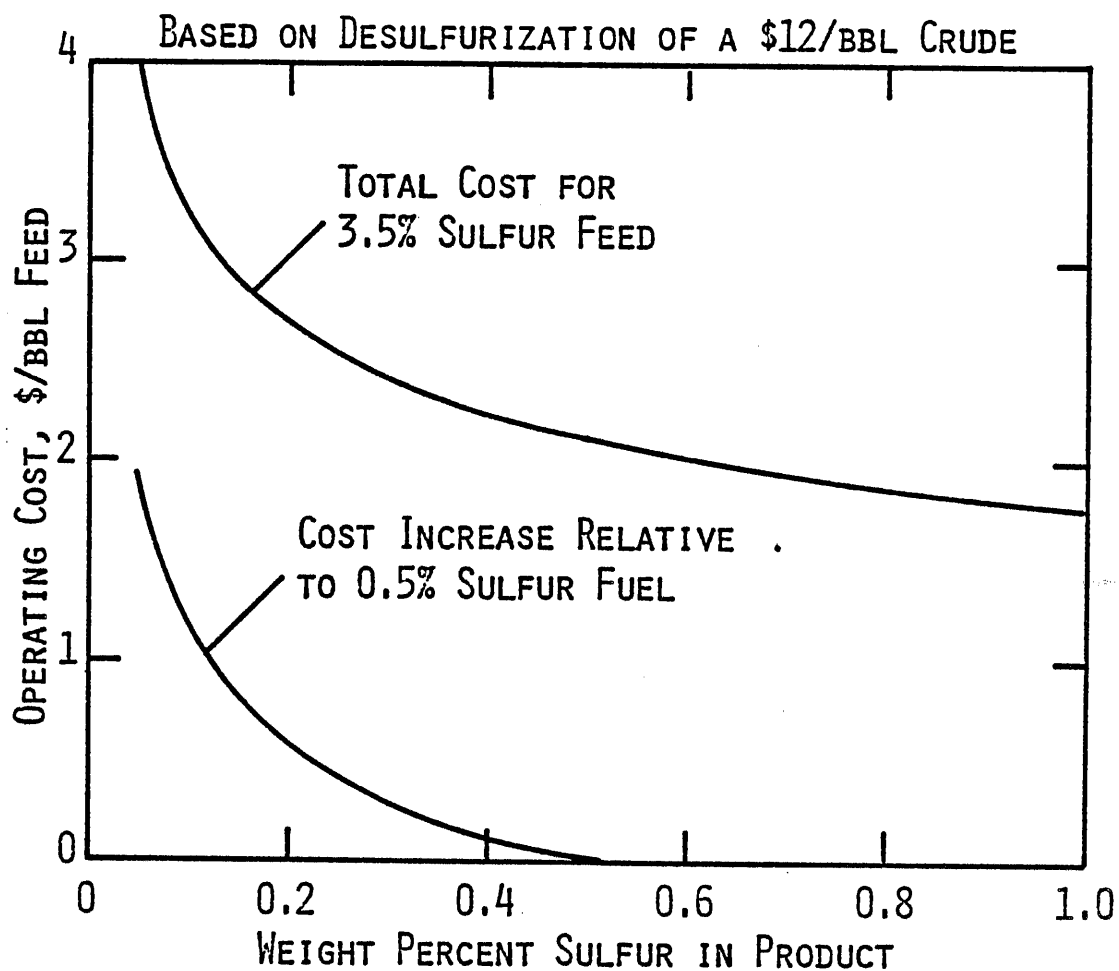


FIGURE F-12. COST OF DESULFURIZING 3.5% S TOPPED CRUDE AS A FUNCTION OF PRODUCT SULFUR CONTENT IN 1975.

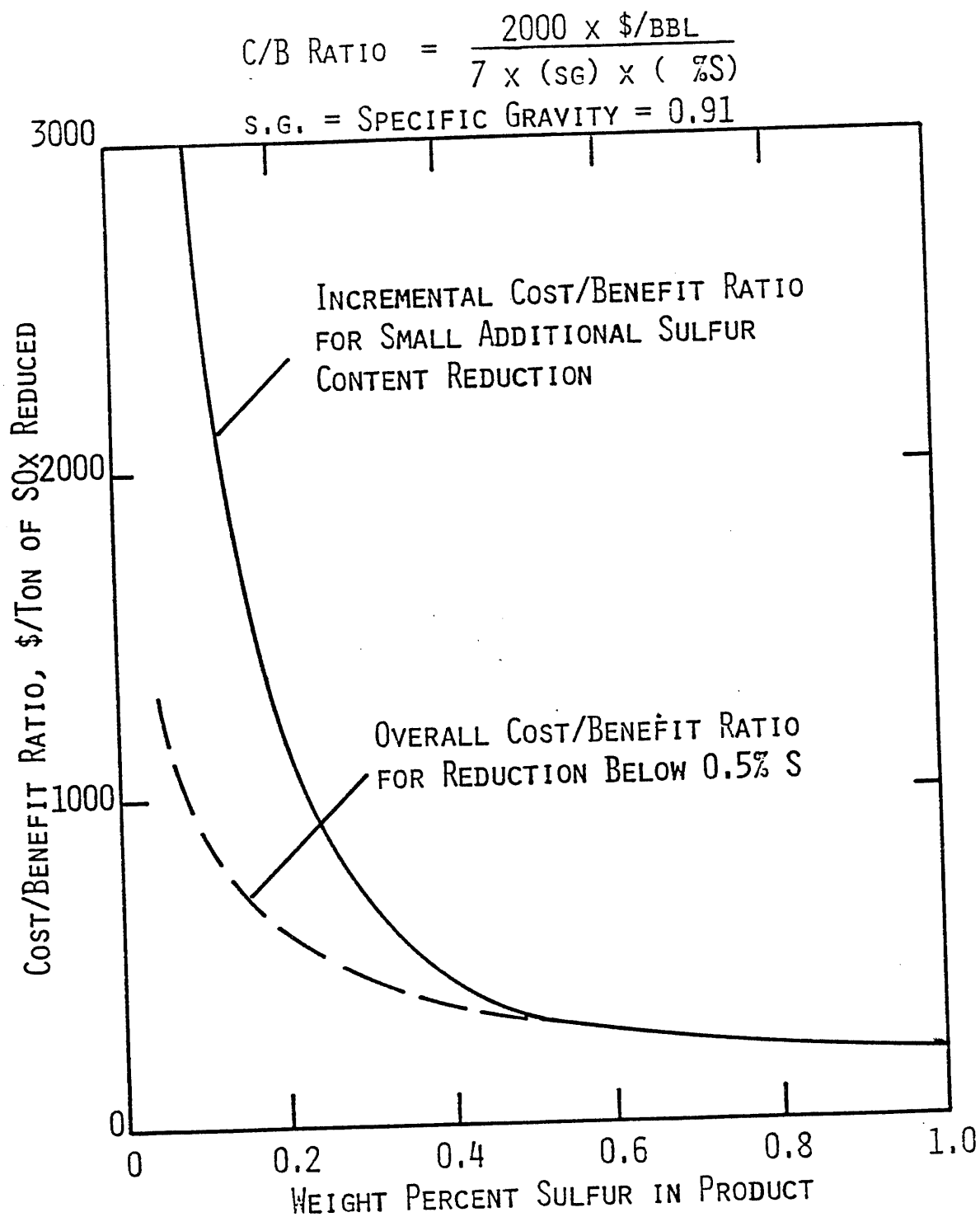


FIGURE F-13. COST/BENEFIT RATIO FOR FUEL DESULFURIZATION.

In view of the uncertainty in costs and the steep rise of the incremental C/B ratio curve at low levels, desulfurization to the 0.2% S level is believed to be a practical limit for cost effective reduction. In addition, data on existing desulfurization processes do not indicate residual oil product sulfur levels less than 0.1% S are currently practical. For this reason, and considering a practical margin, the lowest level of fuel sulfur achievable on a cost effective basis with existing technology is believed to be 0.2% S. The cost/benefit ratio for a reduction from 0.5% sulfur to 0.2% sulfur would be \$600/ton at a cost of \$0.57/barrel and the reduction in SOx emissions would be about 1.0 ton per 1000 barrels of oil burned.

REFERENCES

55. Semrau, Konrad, "Controlling the Industrial Process Sources of Sulfur Oxides," Sulfur Removal and Recovery From Industrial Processes, Adv. in Chem. Series #139, 1975.
56. Rall, H. T., et al., "Sulfur Compounds in Crude Oil," Bu Mines Bulletin 659, 1972.
57. Manderson, M. C., "The Emerging Sulfur Outlook," AIChE National Meeting, Nov. 1975.
58. "Environmental Assessment Study Proposed Sale of Federal Oil and Gas Leases Southern California Outer Continental Shelf - Executive Summary," Dames and Moore, for Western Oil and Gas Association, October 1974.
59. Thompson, C. J., et al., "Analyzing Heavy Ends of Crude," Hydrocarbon Processing, pp. 123-30, Sept. 1973.
60. Dooley, S. E., et al., "Analyzing Heavy Ends of Crude," Hydrocarbon Processing, pp. 187-194, November 1974.
61. Amero, R. C., et al., "Hydrodesulfurized Residual Oils as Gas Turbine Fuels," ASME Technical Division Paper No. 75-WA/GT-8, November 1975.
62. Bridge, A.G., et al., "Chevron Isomax Processes Desulfurize Arabian Heavy Residue," AIChE National Meeting, New Orleans, March 1973.
63. Scott, J.W. and A. G. Bridge, "The Continuing Development of Hydrocracking," Origin and Refining of Petroleum, Adv. Chem. Series 103, Amer. Chem. Soc. 1971.
64. "Here's How Residual Oils are Desulfurized," Oil and Gas Journal, 90-92, May 26, 1975.
65. Billon, Alain, et al., "Cleaning Up the Bottom of the Barrel," Combustion, May 1975.
66. Aalund, Leo, R., "Desulfurization: Hallmark of Huge Social Expansion," Oil and Gas Journal, 71-79, April 7, 1975.
67. Reed, E. M., et al., "Isomax Routes to Low-Sulfur Fuel Oil," National Pet. Refineries Association, Annual Meeting, San Antonio, Texas, March 1972.

68. Nelson, W. L., "1973 Manufacturing Costs of Products," Oil and Gas Journal, June 2, 1975.
69. Nelson, W. L., "Methods Suggested by Accountants," Oil and Gas Journal, May 5, 1975.
70. Nelson, W. L., "How Do Prices Compare With Manufacturing Costs," Oil and Gas Journal, Nov. 17, 1975.
71. Nelson, W. L., "What Will Products Cost in 1975-78," Oil and Gas Journal, Oct. 13, 1975.
72. Nelson, W. L., "Value (of Products) by Alternative Use," Oil and Gas Journal, June 23, 1975.
73. Nelson, W. L., "Indexes For Projecting Manufacturing Costs," Oil and Gas Journal, Nov. 3, 1975.
74. Nelson, W. L., Guide to Refinery Operating Costs, 2nd Ed., Petroleum Publishing Co., Tulsa, Oklahoma, 1970.
75. Meredith, H. H., Jr., "Desulfurization of Caribbean Fuel," 60th Annual Meeting Air Pollution Control Association, Cleveland, Ohio, June 1967.

Blank Page

APPENDIX G

COMBUSTION SOURCES

TABLE OF CONTENTS

	<u>Page</u>
G-1.0 INTRODUCTION	G-1
G-2.0 ELECTRIC UTILITY BOILERS AND TURBINES	G-3
G-3.0 PETROLEUM INDUSTRY COMBUSTION SOURCES	G-20
G-4.0 COMMERCIAL, INSTITUTIONAL, AND INDUSTRIAL BOILERS	G-28
G-5.0 DOMESTIC AND SMALL COMMERCIAL/INDUSTRIAL SOURCES	G-32
G-6.0 INTERNAL COMBUSTION ENGINES	G-34
G-7.0 CONCLUSIONS	G-35
REFERENCES	G-37

Blank Page

APPENDIX G

COMBUSTION SOURCES

G-1.0 INTRODUCTION

Stationary sources of sulfur oxides emissions from combustion include electric utility boilers, petroleum refinery boilers and heaters, internal combustion engines and commercial, institutional, and industrial boilers and heaters. Utility boilers have long been recognized as a major source of SOx emissions because of the very great quantities of fuel burned. Tests of all these combustion devices have consistently demonstrated that for gaseous and liquid fuels the sulfur contained in the fuel is completely converted to sulfur oxides, as illustrated in Ref. 76. For solid fuels a portion of the sulfur may be retained in the ash withdrawn from the furnace bottom. Fuels with these properties are not used in the Basin except in cement kilns.

Control techniques employed to limit sulfur oxides emissions from Basin combustion sources have consisted almost entirely of limitation of the fuel sulfur content. As low-sulfur fuels are in increasingly shorter supply, other methods such as flue gas desulfurization are now coming into increased use on coal-fired devices and may become economically feasible for the larger basin oil-fired devices.

The nature of inventory for SOx emissions from combustion sources resolves primarily to an inventory of fuel consumption and fuel sulfur content and therefrom emissions are readily defined. The major tasks in assembling an accurate inventory and projection involve the fuel type usages, fuel use projections, and cost effectiveness of reduction techniques.

In establishing test priorities for the test program, the substantially higher uncertainty and process variability of the material processing devices as compared with combustion sources led to the decision that tests of most combustion sources would be unproductive. With regard to establishing emissions of total sulfur oxides it is only necessary to know the fuel use rates and sulfur contents from which emissions can be

determined as discussed in Appendix A. One possible area where further test data could have been beneficial was that of SO_3 emissions. The fractions of the fuel sulfur that are emitted as SO_2 and SO_3 are not directly determinable as is the total SO_x . Based on an assessment of LAC APCD data and other data obtained by KVB, it was determined that little improvement in the correlation between SO_2 and SO_3 as a function of fuel type, combustion equipment and operating conditions could be achieved, with the resources available in this program, as compared with assuming an average conversion of SO_x to SO_3 at about 3% by volume.

Three combustion sources burning petroleum processing waste gases were tested. For one device, a refinery odor abatement incinerator, no previous test data were found and waste gas sulfur content was unknown. The other two devices, oil field vapor phase reactors representative of eight devices at one facility, had been previously tested but waste gas sulfur content was not routinely reported. The tests were conducted primarily to verify that waste gas H_2S content was relatively constant as so indicated by the unit operators.

G-2.0 ELECTRIC UTILITY BOILERS AND TURBINES

Utility boilers constitute one of the most clearly definable device categories. There are five utility companies in the Basin having a total of 70 steam-powered generating units that are currently active. In addition, there are 11 gas turbine peaking systems consisting of from one to eight gas turbines, all of which, in a given system, are operated simultaneously. All of these devices are required to operate on liquid fuels of not more than 0.5% sulfur or on gaseous fuels of not more than 50 grains per 100 cubic foot (15 grains/100 CF if burning natural gas). In San Bernardino County, regulations allow control devices equivalent to the use of 0.5% sulfur oil and in Riverside, equivalent to regulated gas fuel. (New Southern Calif. APCD rules allow this in all counties.)

G-2.1 Utility SOx Emission Inventory

The inventory for 1974 emissions of SOx was determined directly from monthly reports of fuel use including quantities used, sulfur content and specific gravity provided to county APCD's by the utilities. This fuel use is in many cases reported for an entire station consisting of several boilers. It was therefore not possible to directly determine the emissions of each individual boiler but this is not as significant a problem as with NOx, for example, where NOx emissions vary substantially from unit to unit and with load. For purposes of computer data base management, each utility boiler was apportioned a quantity of fuel in proportion to the total reported station fuel use by the relative heat inputs established during the previous ARB study of NOx emissions adjusted to reflect the 1974 fuel use. Final inventory computer tabulations of utility emissions agree within 3% with the emission based on fuel reports for annual 1974 emissions.

The relative level of SO₃ emissions as a percent of total SOx was taken as 3% by volume. Actual emissions vary over the range of less than 1% to over 7% as was indicated in Figure 2-1 of Section 2.0 in this report.

Additional data as a function of fuel sulfur content is shown in Figure G-1 including LAC APCD utility boiler source test data by the LAC APCD dry filter test method (Ref. 77) and data obtained for EPA by KVB on

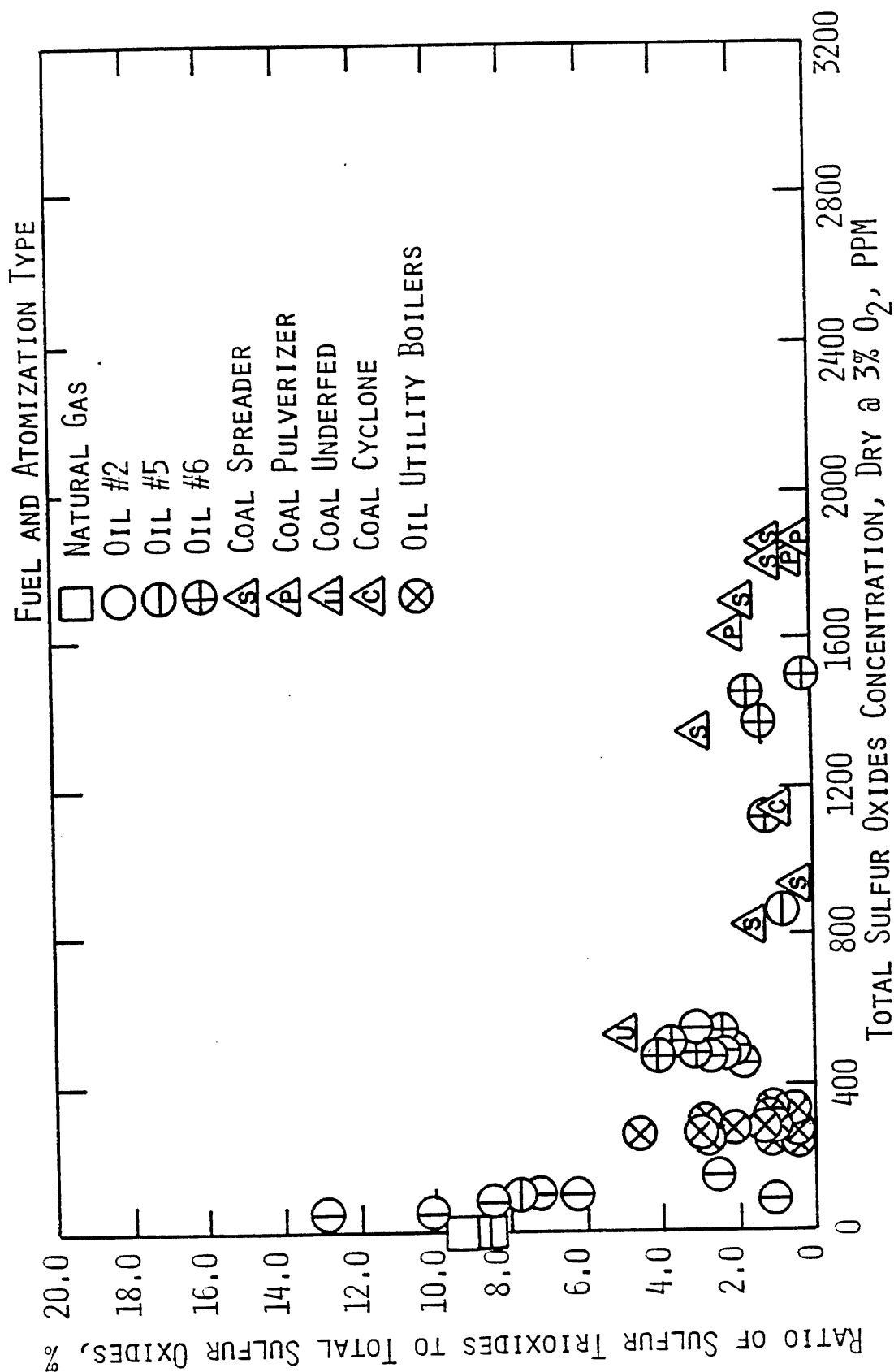


FIGURE G-1. RATIO OF SULFUR TRIOXIDES TO TOTAL SULFUR OXIDES AT BASELOAD AS A FUNCTION OF TOTAL SULFUR OXIDES MEASURED FOR INDUSTRIAL BOILERS (REF. 41) AND UTILITY BOILERS (REF. 47).

industrial boilers (Ref. 76) with the use of the Shell-Emeryville absorption-titration method. At the 0.5% sulfur level, this data indicates an average of 3% conversion adequately represents the data for fuel oil combustion. For individual units, however, the range can be from less than 1% to over 4%. At very low sulfur contents as occur with natural gas higher conversions are indicated. However the test method accuracy at less than 50 ppm of SO_x is questionable as SO₃ levels decrease below 1 - 2 ppm. Unpublished studies of chemical kinetics of SO₃ formation conducted by KVB indicate that there is no kinetic reason to explain an increase in SO₃ as total sulfur level decreases.

Statistical analysis of the test data of Figure G-1 indicates that above 50 ppm SO_x, the percent SO₃ is not a definable function of fuel sulfur. Accordingly a 3% conversion for all combustion sources was assumed.

The resultant 1974 inventory of SO_x and SO₃ emissions from utility boilers and turbines is presented in Table G-I. Utility units in Los Angeles County contribute 64% of Basin annual utility SO_x emissions. Two stations in Ventura County emit 18%, followed by stations in San Bernardino County emitting 10%, and in Orange County emitting 8%. There are no utility stations in the Basin portion of Riverside or Santa Barbara Counties. The three largest generating stations together contribute 53% of Basin emissions.

Projected emissions for 1975, 1976, and 1980 have been formulated based on electric production growth and fuel type availability projections employed for similar projections of NO_x emissions (Ref. 1). Projections for Southern California Edison (SCE) were based on a gas fuel availability of 8% in 1975 and 1% in 1980 (Ref. 78). Gas availability in 1976 was assumed at the 1980 level. Projected generation growth is estimated by SCE to be 4.5% annual average from 1973 to 1975 and 4.6% annual average from 1973 to 1980. Projections for the Los Angeles Department of Water and Power were based on projected station capacity factors obtained from that utility (Ref. 79). Because of recent demand reductions and the availability of power from outside the South Coast Basin, the generation

TABLE G-I

UTILITY SOX EMISSIONS FOR 1974

Station (County)	Station Capacity Mw	Total SOx, Tons as SO ₂ /Day		SO ₃ , Tons as SO ₃ /Day*	
		Aug	Dec	Aug	Dec
<u>Southern California Edison</u>					
Ormond Beach (Vt)	1,500	30.04	25.64	1.127	0.961
Mandalay (Vt)	551	9.81	13.32	0.368	0.499
Huntington Beach (Or)	991	11.40	25.03	0.427	0.939
Etiwanda (S. Bn)	1,025	12.11	23.62	0.455	0.886
Highgrove (S. Bn)	156	0.02	0.01	0.0	0.0
San Bernardino (S. Bn)	126	0.08	4.89	0.004	0.183
Alamitos (IA)	2,071	32.40	46.61	1.215	1.748
El Segundo (IA)	1,010	12.72	25.48	0.476	0.955
Redondo (IA)	1,590	0.19	22.19	0.008	0.830
Total SCE	9,020	108.77	186.79	4.080	7.001
<u>Los Angeles Dept W&P</u>					
Haynes (IA)	1,427	16.06	46.06	0.602	1.727
Harbor (IA)	509	0.0	2.07	0.0	0.078
Valley (IA)	550	0.0	6.47	0.0	0.243
Scattergood (IA)	360	0.02	13.32	0.0	0.500
Total LADWP	2,846	16.08	67.92	0.602	2.548
Burbank P.S. (IA)	197	1.97	4.05	0.073	0.153
Glendale P.S. (IA)	189	2.44	4.99	0.092	0.186
Pasadena DWP (IA)	225	2.26	4.16	0.085	0.156
BASIN TOTALS	12,447	131.52	267.91	4.932	10.044
					6.456

*Based on 3% volume conversion of SOx to SO₃.

rate decreases from 1973 to 1975 at an annual rate of 10% and then remains constant to 1980. Gas availability in 1975 is projected to be 6% and drops to zero for 1976 through 1980. Projected growth rates for the three remaining utilities for 1974 through 1980 were taken at 4% per year based on estimates from each utility (Refs. 80 - 82). Gas availability was taken as 10% in 1975 and 1% in 1976 through 1980. New units being added were included in the projections. These units are all gas turbine combined cycle systems, and in some cases replace boilers in the 1974 inventory.

Projected annual oil use by all utilities will increase from 46 million barrels in 1974 (actual reported use) to 83, 92, and 106 million barrels in 1975, 1976, and 1980 respectively. The oil use for the various utilities is compared with total fuel requirements in Figure G-2, illustrating the sharp increase expected in 1975. Resultant SO_x and SO₃ annual average daily emissions are presented in Table G-II based on the assumption that fuel sulfur contents remain at 1974 levels of about 0.4 to 0.45% S by weight. The projected oil usage, at roughly double the 1974 levels, is believed to be the highest levels that could be expected. The effects of energy conservation and importation of power from outside the Basin could result in fuel use that is as much as 25% lower than the projected usage. In addition, the upward trend from 1976 to 1980 cannot be extended beyond 1980 since power imports from outside the Basin are expected to result in reduced fuel use and emissions.

Projections have not been made for summer and winter average daily emissions as specific patterns are not yet known. However by 1976 with gas fuel use nearly completely curtailed the utility SO_x seasonal patterns will disappear except for load fluctuations and daily average emissions will be similar for both summer and winter days. While annual emissions will increase 230% from about 172 tons/day to 404 tons/day from 1974 to 1980, summer daily emissions will increase 280% from 131 tons/day to about the same 400 ton/day level. Winter emissions, based on nearly 100% oil use already, will rise only 145% as the result only of load growth.

These projections are based on maintenance of the 0.44 sulfur 1974 level. At 0.5% S, 1980 emissions would be 459 ton/day. If higher sulfur fuels are the only fuels available, SO_x emissions will increase in direct proportion to sulfur content. Unless some alternate control methods are employed, utility emissions of SO_x could well exceed 1000 tons/day in 1980.

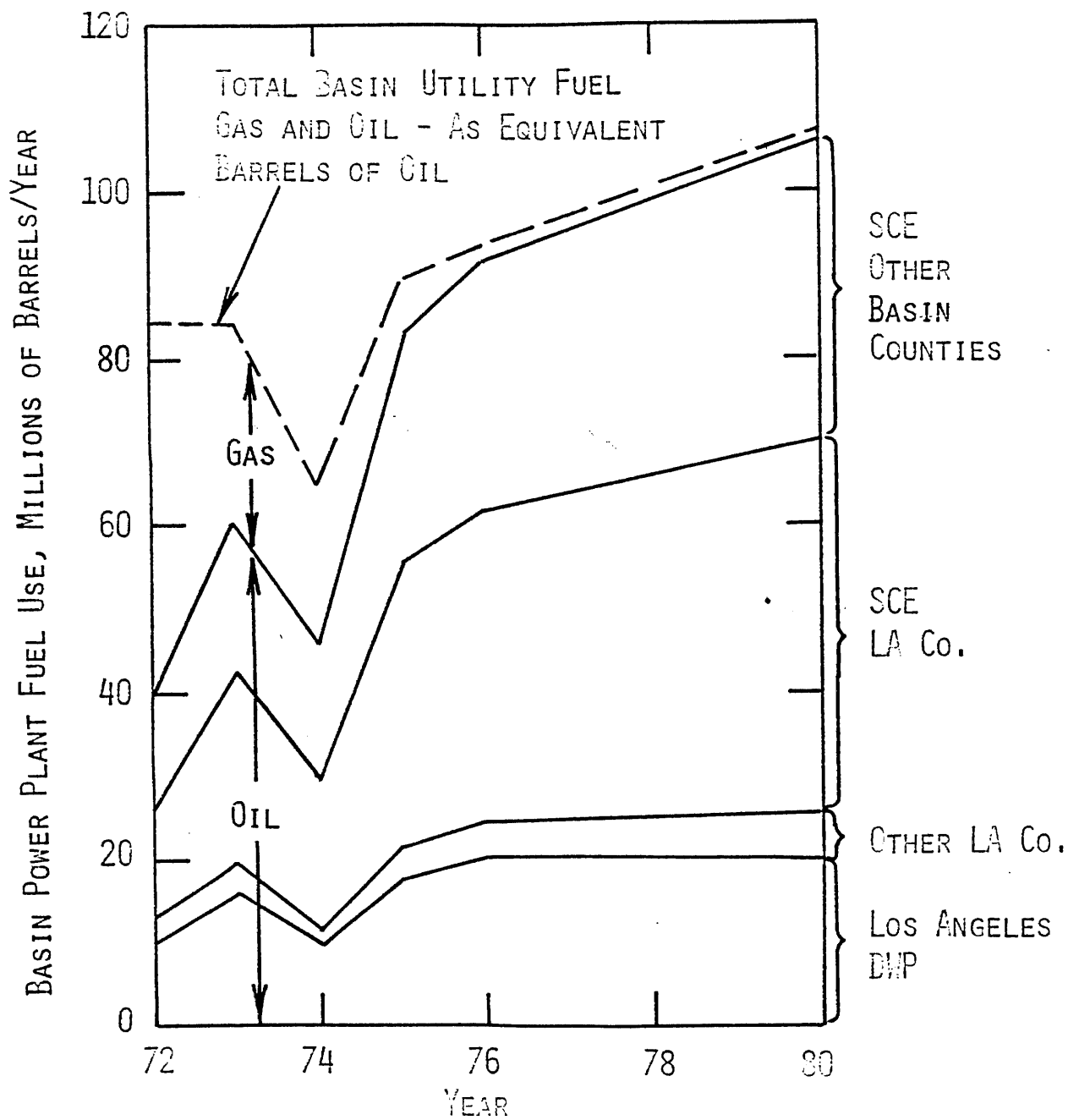


FIGURE G-2. PROJECTED FUEL USE BY SOUTH COAST AIR BASIN POWER PLANTS.

TABLE G-II

PROJECTED SOX AND SO₃ EMISSIONS FOR ELECTRIC UTILITIES
IN THE SOUTH COAST AIR BASIN

	SOx, Tons as SO ₂ /day*				SO ₃ , Tons as SO ₃ /Day**			
	1974	1975	1976	1980	1974	1975	1976	1980
Southern California Edison								
Ventura County	32	52	59	71	1.19	1.95	2.21	2.66
Orange County	13	21	24	29	0.49	0.79	0.90	1.09
San Bernardino County	17	28	32	38	0.65	1.05	1.20	1.43
Los Angeles County	68	127	143	171	2.53	4.76	5.36	6.41
Total SCE	130	228	258	309	4.86	8.55	9.68	11.59
Los Angeles DWP	36	72	77	77	1.34	2.70	2.89	2.89
Burbank P.S.	2	5	5	6	0.08	0.19	0.19	0.23
Glendale P.S.	2	5	5	6	0.09	0.19	0.19	0.23
Pasadena DWP	2	5	5	6	0.09	0.19	0.19	0.23
BASIN TOTALS	172	315	350	404	6.46	11.82	13.13	15.15

* Assumes 1974 fuel sulfur contents. 1980 emissions* at 0.5% S would be 459 tons of SOx/day.

** Assumes 3% by volume of SOx as SO₃.

G-2.2 Utility SOx Reduction Potential

All utility boilers in the South Coast Air Basin are currently under regulations to limit sulfur content to no more than 0.5% for oil. There is no size distinction on these limits as in the case of NOx, so no potential reductions related to extension of regulation limits can be made.

The real concern that must be addressed is related not to 1974 emissions but to the projected substantial future increases. Three possibilities are considered as related to fuel oil requirements for 106 million barrels in 1980 in the event of most certain complete natural gas curtailment:

1. Fuel oil at 0.5% S maximum is available at 106 million barrels/y.
2. Fuel oil at 0.5% S maximum is available at 1974 level of 46 million barrels/y, and 60 million barrels of high sulfur oil are burned.
3. All 106 million barrels of fuel supplied as high sulfur oil.

Possibility number 1 is the one on which projections were based in the previous section indicating growth of 232 tons/day from 1974 (172 t/d) to 1980 (404 t/d). If this growth must be restricted then one practical control method (except, of course, more natural gas) is to further restrict the fuel sulfur content. Utility fuel oil sulfur content in 1974 averaged about 0.44%. Sulfur content would have to be limited to 0.2% to maintain 1974 levels and limit the 232 ton/day increase. Appendix F indicates that the differential cost of 0.2% compared to 0.5% S oil is about \$.60/Bbl (1975 basis). At this level the cost/benefit ratio of this reduction would be \$600 per ton (See Appendix F for C/B ratio for fuel desulfurization.) of SOx reduced for prevention of the 232 ton/day increase. This is assuming that 0.44% sulfur oil is still available and only needs to be desulfurized further to below 0.2% S.

In the second possibility noted above, low sulfur fuel oil at 0.5% S would be available only in amounts equal to about the 1974 level (46 million barrels) while about 106 million barrels will be required in 1980. Assuming 46 MMBBL are burned at 0.44% S and 60 MMBL are burned

at 3.4% S (worst case - Arabian oil) then the growth, instead of 232 tons/day would be 1800 tons per day for a total stationary source 1980 emission of 1950 tons/day. However, regulations already exist that would require sulfur removal to at least the 0.5% level. The cost for that reduction is about \$2.10/BBL (1975 level) assuming 3.4% S oil (a cost/benefit ratio of \$215/ton SO_x). Only the additional cost to reduce from 0.5% to 0.2% sulfur should be considered for the cost effectiveness of a 0.2% level requirement. This incremental cost is \$0.60/BBL for a cost/benefit ratio of \$600/ton SO_x. The combined cost/benefit ratio for the 46 MMBBL at 0.44% S to 0.2% and 60 MMBBL at 0.5% to 0.2% remains at \$600/ton SO_x for the same reduction of 232 tons/day.

Consideration of the third possibility mentioned, total use of high sulfur fuel oil, leads to essentially the same conclusion.

In effect, all three possibilities result in essentially the same cost/benefit ratio regardless of the fuel used since only the costs below the 0.5% sulfur level are considered.

The actual total annual cost to the utilities of course varies considerably for each of these possibilities as shown below:

1. 106 MMBBL at \$0.6/BBL = \$64 million
2. 46 MMBBL at \$0.6/BBL = 28 million
60 MMBBL at 2.70/BBL = 162
\$ 190
3. 106 MMBBL at \$2.70/BBL = \$286 million

The practicality and methods for residual fuel desulfurization are discussed in Appendix F. It would appear that this is a practical approach at 50-100,000 BBL/day plant size. The 0.2% S level is considered above only in terms of a lower limit of existing cost effective technology for residual fuels. The requirement, if any, for reduction to a level between 0.5 and 0.2% S can only be established by proper consideration of air quality requirements.

The alternative to fuel desulfurization is to allow the use of high sulfur oil and install flue gas desulfurization scrubbers. The subject of scrubbers is a highly controversial subject that has been widely discussed; mainly in connection with coal-fired plants. There is extensive literature on scrubbing technology, costs, reliability and operational status. It was decided that inclusion of yet another "Summary of Flue Gas Desulfurization" in this report would be unproductive as processes and costs are changing rapidly and current journals are the best references for most recent information. The "Wet Scrubber Newsletter" published monthly by the McIlvaine Company, Northbrook, Illinois, was found to contain the most recent information. Cost data developed by TVA (Ref. 83) represents the most definitive costing found in the literature for the five most promising scrubbing systems:

1. Limestone slurry - with sludge disposal
2. Lime slurry - with sludge disposal
3. Magnesia slurry - sulfuric acid production
4. Catalytic oxidation (Cat-Ox) - sulfuric acid production
5. Sodium scrubbing - sulfur production

Cost data are developed for coal and oil fired units in the range of 200 to 1000 Mw for both new and existing power plants.

For oil-fired boilers there are only two known installations in the United States:

1. Boston Edison Mystic 6, 155 Mw
Magnesia slurry, regenerative system, 2-2.5% S oil
2. Key West Utility Stock Island, 37 Mw
Limestone system, 2.5% S oil

The Boston Edison unit was built as a research project for a two-year demonstration program. The project was completed March 1974 and conclusions were that operation was satisfactory (Ref. 84). The magnesia process involves scrubbing with an MgO slurry. The MgO reacts

with SO_2 to form MgSO_3 . The MgSO_3 is regenerated by calcining and produces a stream of concentrated SO_2 which is sent to a sulfuric acid plant. There is, therefore, no solid waste disposal problem and sale of the acid can significantly reduce operating costs. The Key West system is not currently in operation (Ref. 85).

The majority of coal-fired scrubbers are employing lime or limestone systems and generate a sludge that requires disposal. There are still many unresolved questions regarding environmental acceptability of sludge disposal. While cost data is developed below for installation of scrubbers on Basin utility boilers, a very detailed study of the full environmental impact on the Basin area would be required before wide-spread use of these systems could be implemented. In addition, as environmental assessment, design, and construction of these systems would require from two to five years, it is unlikely that installation of scrubbers would be effective in limitation of SO_x emissions in the 1979-1980 critical period now forecast.

Most systems proposed for FGD achieve at least 90% SO_2 removal. Therefore, the achievable emission equivalent to burning desulfurized oil is one-tenth the level of sulfur in the oil actually burned. To achieve the equivalent of burning 0.2% S oil, a boiler with a scrubber is limited to firing with 2% S oil maximum. Since future crude supplies are expected to produce fuel oils ranging up to 4% S, some desulfurization may still be necessary even if scrubbers are installed on Basin power plants. Cost analysis in comparison with complete fuel desulfurization then involves a trade-off of partial desulfurization plus scrubbing versus full desulfurization. Such a study has been conducted by the California Air Resources Board staff (Ref. 86) based on costs of Reference 83. The conclusion of this study was that for large boilers

(500 Mw), fuel desulfurization to 1% S plus scrubbing was technically feasible for obtaining an emission rate equivalent to burning oil desulfurized to 0.1% S. The study concluded that this approach based on the limestone process was more cost effective than full fuel desulfurization to 0.1% S. The cost data of Reference 96 indicate the limestone process has lowest operating costs for firing at 2.5% S. For 1% S fuel the magnesia process has a slightly lower operating cost.

Recent cost estimates (Ref. 85) indicate that the currently higher prices of sulfuric acid and sulfur will significantly reduce operating costs of the magnesia and cat-ox processes below that of lime or limestone systems. In view of this development and the fact that the capital investment for the magnesia process is about 1/2 that of the cat-ox system (Ref. 83), data for the former will be used here.

The operating costs of scrubbing systems installed on existing plants is estimated to be about 25% higher than for similar systems installed on new plants (Ref. 83). Capital investment and operating costs were developed from Reference 83 for installation of magnesia systems on existing oil-fired units. Figure G-3 shows these costs for the 200-1000 Mw range and for firing 1 to 4% S oil. The data is plotted in carpet fashion for ease in interpolation. Application of this data to the 24 largest Basin power plants is presented in Table G-III. Total capital investment is \$358 million, an average of \$43/kw firing 2% S oil. Annual operating costs range from 1.7 to 2.5 mills/kwh and total annual cost is \$93 million. Although 2% S oil is assumed, reductions in SOx emissions are based only on the reduction below the 0.5% S level and the reduction is 176 tons/day. On this basis the cost benefit ratio ranges from \$1166/ton to \$1718/ton of SOx removed below the 0.5% S level. The average system operating cost per barrel of 2% S fuel oil burned is \$1.45/bbl. This cost and the cost/benefit ratio can be

EXISTING OIL-FIRED UNIT
90% SO₂ REMOVAL

G

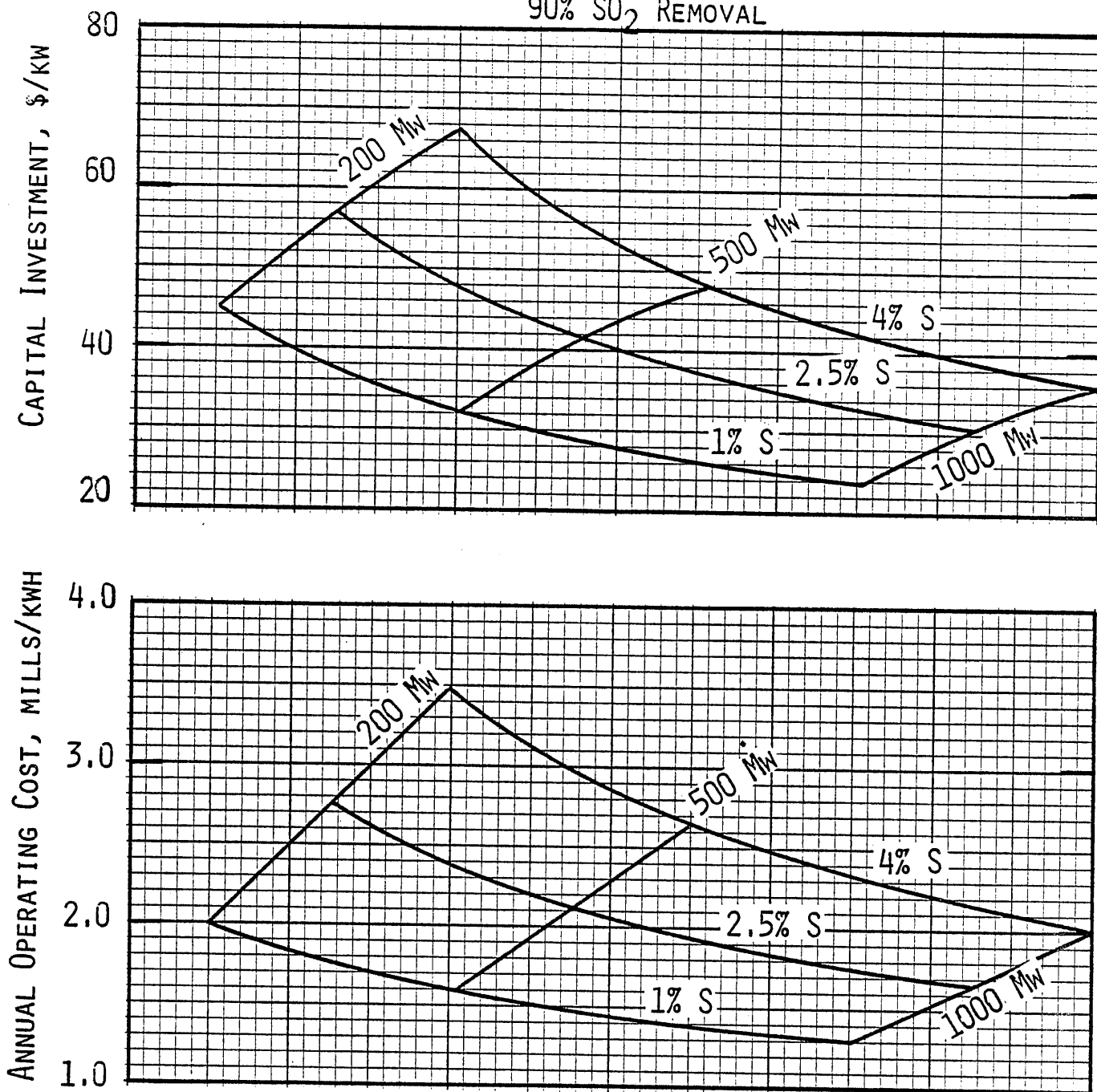


FIGURE G-3. CAPITAL INVESTMENT AND OPERATING COSTS FOR
MAGNESIA SCRUBBING SYSTEM.

5802-432

TABLE G-III

ELECTRIC UTILITY SCRUBBER COSTS
24 LARGEST SOUTH COAST AIR BASIN STEAM BOILERS

Size, Mw	Size Group, Mw	Generation 60% Capacity 8760 H/Y 10 ⁹ KWH/Y	(1) Scrubber Investment \$MM	(1) Operating Cost mills/KWH	Annual Cost \$MM/Y	(2) SO ₂ Reduction tons/yr	Cost/ Benefit Ratio \$/ton	Cost \$/bbl
750	1,500	7.884	48	1.7	13.4	11,500	1,166	1.16
750								
480								
480	1,920	10.090	76	1.9	19.2	14,700	1,306	1.30
480								
480								
330	2,640	13.875	119	2.2	30.5	20,600	1,480	1.51
330								
320								
320								
320								
320								
350								
350								
245								
245								
242	2,272	11.940	115	2.5	29.9	17,400	1,718	1.71
240								
225								
215								
215								
215								
215								
215	8,332	43.790	358	2.1	93.0	64,200	1,449	1.45
215								
			(Avg. 43 \$/kw)	Avg.		(176 T/D)		Avg.

(1) Cost data, PB 242541, Magnesia Slurry, Oil Fired, Existing Units, 2.0% S fuel, 90% reduction. Costs not reduced by savings due to burning higher sulfur oil or for byproduct credit. Cost basis 1975.

(2) SO₂ Reduction based on 60% reduction from SOx emission rates with 0.5% S fuel. (90% reduction for 2.0% S fuel.)

significantly influenced by a number of factors. Capital investment can be increased over 100% by various increased costs indicated in Reference 83 as modifications to the project scope. This effect on annual operating cost, and the influence of fuel sulfur content are illustrated in Figure G-4 in comparison with costs for full fuel desulfurization as developed in Appendix F. The base case operating cost of the FGD system alone decreases with decreased fuel sulfur content (constant 90% system SO_2 removal rate). Firing a 1% S oil would incur a cost of \$1.17/bbl as compared with a cost of \$1.85/bbl for 4% S oil. These base costs are significantly lower than the cost to desulfurize a 3.5% oil. However to place the costs on a comparable basis, scrubbing it to an equivalent 0.1% S level requires firing 1% S oil at 90% removal. Addition of the cost to desulfurize oil from 3.5% to 1% S increases total operating costs to a level very close to the straight desulfurization cost. Addition of increased capital charges for accelerated construction and an escalation of utility fuel cost from the \$9.66/bbl used in Reference 96 to \$16/bbl (as a typical example of but one area of possible escalating cost) results in a total cost that significantly exceeds the straight desulfurization costs. In view of this and other cost factors the actual cost of an FGD system can only be determined for each installation and specific judgements for each case would have to be made regarding the relative merit of combined flue gas and fuel desulfurization versus straight fuel desulfurization. The main conclusion is that both methods appear to be within the realm of existing technology and offer alternate approaches to the reduction of Basin SO_x emissions.

The cost/benefit ratios shown in Table G-III were based on scrubber costs alone assuming 2% S fuel is available at no cost differential compared with 0.5% S fuel. Adding a cost of \$1.05/bbl to desulfurize 3.5% S fuel to 2% S would increase the average cost/benefit ratio of FGD

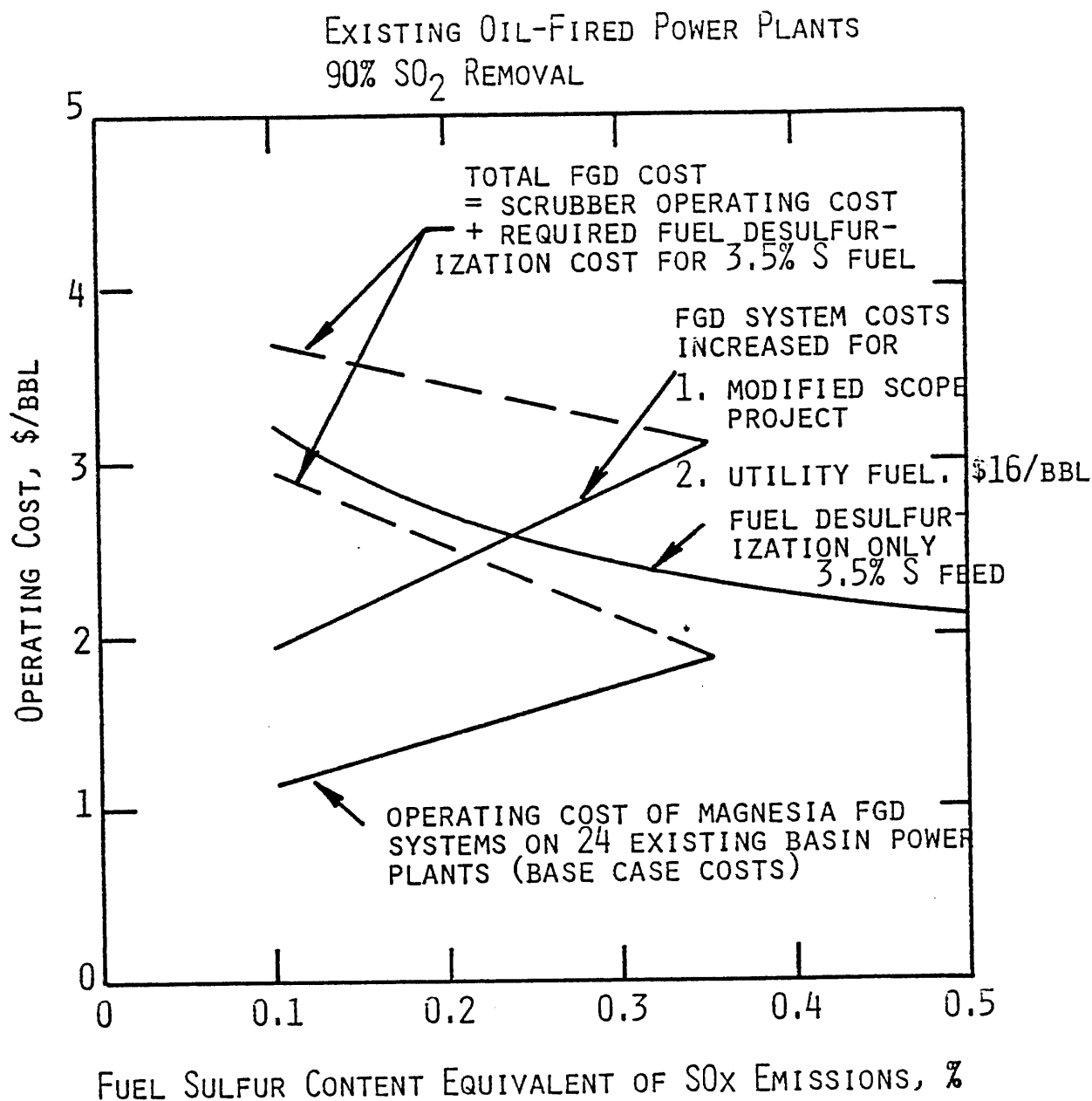


FIGURE G-4. COST COMPARISON OF FLUE GAS DESULFURIZATION AND FUEL OIL DESULFURIZATION.

from \$1449/ton to \$2500/ton (\$3.45/bbl). With higher possible scrubber operating costs as indicated in Figure G-4 the cost/benefit ratio would increase to \$3,450/ton. However, since 0.5% S fuel would not have to be bought, a \$2.10/barrel cost should be credited to the FGD system resulting in a net cost of only \$0.40/bbl or \$400/ton for a reduction of 176 tons/day, assuming base case costs. On the basis of possible higher scrubber system costs as indicated in Figure G-4, the cost benefit ratio, with 0.5% sulfur credit, would be \$1350/ton (\$1.35/bbl) for SO_x reduction to the 0.2% S level equivalent and a total reduction of 176 tons/day. Similarly, at a 0.1% S level equivalent, total cost ranges from \$2.95/bbl to \$3.70/bbl or with 0.5% S credit of \$2.10/bbl, is \$.85-1.60/bbl with a cost effectiveness of \$640-1200/ton for a reduction of 234 tons/day at the 1980 period. Summarizing, in comparison with full fuel desulfurization, at the 0.2% S equivalent level, fuel desulfurization to 2% S plus FGD at 90% SO₂ removal has an estimated cost/benefit ratio of \$400-1350/ton for a potential reduction of 176 tons/day based on application to the 24 largest boilers. Fuel desulfurization only to 0.2% sulfur has a cost/benefit ratio of \$600/ton (Appendix F) with a potential reduction of 176 tons/day for 24 boilers or 220 tons/day for all basin boilers. FGD is therefore concluded to cost from 67 to 225% of fuel desulfurization at comparable emission rate levels. Reduction of the fuel sulfur to 1% S for a 0.1% S equivalent emission with FGD at 90% removal results in a cost benefit ratio of \$640 to 1200/ton for a potential reduction of 234 tons/day for the 24 largest utility boilers.

A more detailed study of the actual costs and trade-off for each individual boiler would probably result in some optimum combination of fuel desulfurization for smaller boilers and scrubbing for larger boilers that would result in the lowest overall basin cost/benefit ratio.

One important final point is the effect of scrubbing on SO₃ emissions. While scrubbing has been demonstrated as very effective for SO₂ removal there was no information found on SO₃ and this should be investigated further.

G-3.0 PETROLEUM INDUSTRY COMBUSTION SOURCES

Combustion sources of SO_x in the petroleum industry include boilers, process heaters, and internal combustion engines in oil refineries and waste gas burners in both refineries and oil field operations. Carbon monoxide boilers used for combustion of oil refinery catalytic cracking waste gas are considered in Appendix H as SO_x emissions result from FCC off gas rather than fuel combustion.

Tests were conducted only on two types of petroleum processing waste gas burners where sulfur contents were unknown.

G-3.1 Petroleum Refinery Fuel Combustion

The predominant fuel consumed in refineries is refinery gas. The distribution of fuels for FY'72 was about 72% refinery gas, 22% natural gas, and 6% oil. During the summer months the fuel was almost entirely a mixture of refinery gas and natural gas, while in the winter about 17% of the fuel was oil. During 1974 these levels remained nearly the same at 69% refinery gas, 23% natural gas, and 8% oil. Total fuel consumption dropped slightly from 32.2 million barrels of fuel oil equivalent (BFOE) in fiscal '72 to 29.7 million BFOE in 1974. Total oil processing capacity for Los Angeles refineries is about 1,060,000 barrels of crude per day (Ref. 13) indicating a fuel requirement of about 8% of crude capacity (8 barrels fuel burned per 100 barrels crude processed). Fuel consumptions should remain relatively constant to 1980 with the exception of a 175,000 barrel/day addition in an existing refinery to produce low-sulfur fuel oil. Preparing an inventory of SO_x emissions for these fuel consumptions requires obtaining fuel usage and sulfur content data. Such data is collected by the LA APCD on a daily basis and has been used as the sole source of data for oil refinery SO_x emissions.

Sulfur contents of fuel oils burned in refineries vary from 0.23% to 0.5% sulfur and average 0.4% (Ref. 12). Refinery gas composition varies widely including sulfur content. Refinery gas is produced as a byproduct of the refining process and without special sulfur removal could yield very high SO_x emissions. However, all refineries in the Basin have installed amine stripping units that remove the sulfur from the fuel gas. The resulting waste gas, mostly H₂S, is processed in

sulfur recovery plants, as discussed in Appendix I, or sulfuric acid manufacturing plants, Appendix J. Refinery gas sulfur content is limited by LA APCD Rule 62 to 50 grains H_2S /100 CF approximately equivalent to 0.15% sulfur by weight (varies as a function of specific gravity). In 1974 the sulfur contents in LA refinery fuel gas varied from 0.03 to over 433 grains H_2S /100 CF but averaged about 7 to 9 grains H_2S /100 CF. Grain contents were derived from LA APCD reported data in terms of tons SO_2 emitted and refinery gas expressed as barrels fuel oil equivalent. Apparently the refineries report gas consumption in MMCF (million cubic feet) and LA APCD converts to BFOE with an assumption of 4500 CF per BFOE. This is equivalent to a heating value of 1400 Btu/CF. Actual refinery gas heating values vary widely, between 1000 and 1600 Btu/CF (6300 to 3940 CF/BFOE) according to gas compositions obtained from refineries during the NOx study (Ref. 1). For this study the LA APCD BFOE values were converted to MMCF with typical heating values provided by the refineries so that SOx computer data base entries in MMCF would be as close as possible to actual values.

Requirements for inventory by location and device type, primarily a distinction between refinery boilers and heaters, the total fuel use must be properly apportioned to the various devices in the computerized data base. In the NOx study (Ref. 1), operating capacity factors and rated heat input rates were determined either on an overall refinery basis or for particular groupings of units, and these values served as the starting point for this program. Refinery gas fuel useage reported to the LA APCD for 1974 was converted from barrels fuel oil equivalent to cubic feet with heating value typical for each refinery. Fuel usage in special devices (CO boiler, ICE) was subtracted from the reported totals. Total energy capacity factors for all heaters and boilers were obtained from total energy consumption in August, December and annual reported fuel use. Summer, winter and annual gas use by gas only units was then determined from the adjusted capacity factors for each device. Gas use by gas units was then subtracted from total gas use to determine summer, winter, and annual oil unit gas use. From the total oil unit gas and total refinery oil (minus any estimated CO boiler oil), overall fractions of summer,

winter and annual oil use were determined and applied to all oil devices uniformly. This assumption, together with the adjusted capacity factors, determines the summer, winter and annual gas and oil use for each oil device. Finally, computer listings of summations of gas and oil use were checked to verify that the total useages equaled the reported useages. Average fuel sulfur contents were determined for each refinery based on reported SOx emissions for each fuel and each device was assigned this average for SOx calculation.

The foregoing procedure insured that total computer data base inventory SOx emissions from fuel combustion for each refinery was equal to reported emissions. These procedures may not necessarily reflect totally accurate emissions from each individual device but this is not a particularly significant problem as group ensemble emissions are of primarily interest for determining device and geographic SOx distributions.

An assumption implicit in this entire procedure is that adequate procedures are maintained by the LA APCD to insure the accuracy of reported values. Because of the high variability in refinery fuel gas properties and probable oil variations, a source test verification would have required sampling many units. Compared with other sources, the level of emissions from refinery fuel combustion is of limited importance and such a survey would have been unproductive.

The total inventory values of SOx and SO₃ emissions from refinery fuel combustion are presented in Table G-IV. SO₃ emissions are based on 3% conversion of SOx to SO₃. Winter emissions are about twice the annual average because of increased fuel oil burning. Summer emissions are due almost entirely to refinery gas consumption.

Projections for oil refinery emissions to 1980 are given in Table G-V and include a return to 1972 fuel consumption rates that were near full capacity and for 1980 the inclusion of a new low sulfur fuel oil facility. Projections are shown both for two levels of natural gas use and for the assumption that all natural gas is curtailed and replaced with 0.5% S fuel oil. For continued gas availability, SOx emissions increase only 15%. With complete gas curtailment, SOx emissions could rise to 50 tons/day by 1980.

TABLE G-IV

SOx EMISSIONS FROM FUEL COMBUSTION IN 1974
FOR LOS ANGELES OIL REFINERIES

	Refinery Gas	Fuel Oil	Natural Gas	Total
1974 Consumption, BFOE	20,448,544 *	2,292,331 *	6,922,094 *	29,662,969 *
Average Sulfur Content	$\frac{7 \text{ gr H}_2\text{S}}{100 \text{ CF}}$	0.40% S by weight	$\frac{0.3 \text{ gr H}_2\text{S}}{100 \text{ CF}}$	--
SOx, tons/yr	1140	2918	13.5	4072
Annual Daily Avg SOx, tons/day	3.12	8.0	0.04	11.15
Summer Daily Avg SOx, tons/day	2.69	0.48	0.05	3.23
Winter Daily Avg SOx, tons/day	2.91	17.4	0.01	20.32
SO ₃ , tons/yr	43	109	0.5	153
Annual Daily Avg SO ₃ , tons/day	0.12	0.30	0	0.42

* BFOE = 4500 CF Refinery gas
= 6000 CF Natural gas
= 42 gallon oil

5802-432

TABLE G- V

PROJECTED SO_x EMISSIONS FROM FUEL COMBUSTION
FOR LOS ANGELES OIL REFINERIES

	1974	1975	1976	1980
<u>1974 Gas Availability, % of Req'd</u>	75	75	75	75
Refinery gas, MMBFOE	20.4	22.2	22.2	23.6
Natural gas, MMBFOE	6.9	7.4	7.4	7.9
Fuel oil, MMBFOE	2.3	2.6	2.6	2.8
Annual Daily Avg SO _x , tons/day	11.2	12.1	12.1	12.9
Annual Daily Avg SO ₃ , tons/day	0.42	0.46	0.46	0.49
<u>No Natural Gas</u> (Replaced with 0.5% S fuel)				
Refinery gas, MMBFOE	20.4	22.2	22.2	23.6
Fuel oil, MMBFOE	2.3	10.0	10.0	10.7
Annual Daily Avg SO _x , tons/day	11.2	47	47	50
Annual Daily Avg SO ₃ , tons/day	0.42	1.8	1.8	1.9
<u>New Gas Supplies Available</u> Gas Availability, %	75	75	53	45
Refinery gas, MMBFOE	20.4	22.2	22.2	23.6
Natural gas, MMBFOE	6.9	7.4	5.6	5.0
Fuel oil, MMBFOE	2.3	7.6	4.9	6.0
Annual Daily Avg SO _x , tons/day	11.2	12.1	21	25
Annual Daily Avg SO ₃ , tons/day	0.42	0.5	0.8	0.9

5802-432

Combustion of fuels at refineries is currently one of the smaller sources of emissions, but could become a much more significant source in the event of complete natural gas curtailment. Methods for reductions of SOx such as flue gas scrubbing appear to be impractical because of the very large number of devices and lack of space for installation. The use of lower sulfur fuel oil in the event of natural gas curtailment is seen as the only practical reduction method. For example, sulfur levels would have to be reduced from 0.5% current levels to under 0.2% to maintain current emission levels. At a cost of \$0.60/barrel to reduce the sulfur content, the cost/benefit ratio would be 600 \$/ton of SO₂ reduction for a total reduction of 28 tons/day (1980 worst case level). Variables affecting desulfurization costs, discussed in Appendix F, could significantly increase this cost.

G-3.2 Miscellaneous Petroleum Industry Sources

In addition to refinery fuel combustion, three other combustion related sources of SOx were identified in this program: internal combustion engines, one refinery odor abatement incinerator, and oil field waste gas burners (termed vapor phase reactors). Internal combustion engines operate on natural gas and as such emit negligible SOx. All engines included in the NOx survey were retained in the SOx inventory but emissions are less than 2 tons of SO₂/year. Gas curtailment would increase emissions to 370 tons/year (1 ton/d) if 0.25% S distillate were burned.

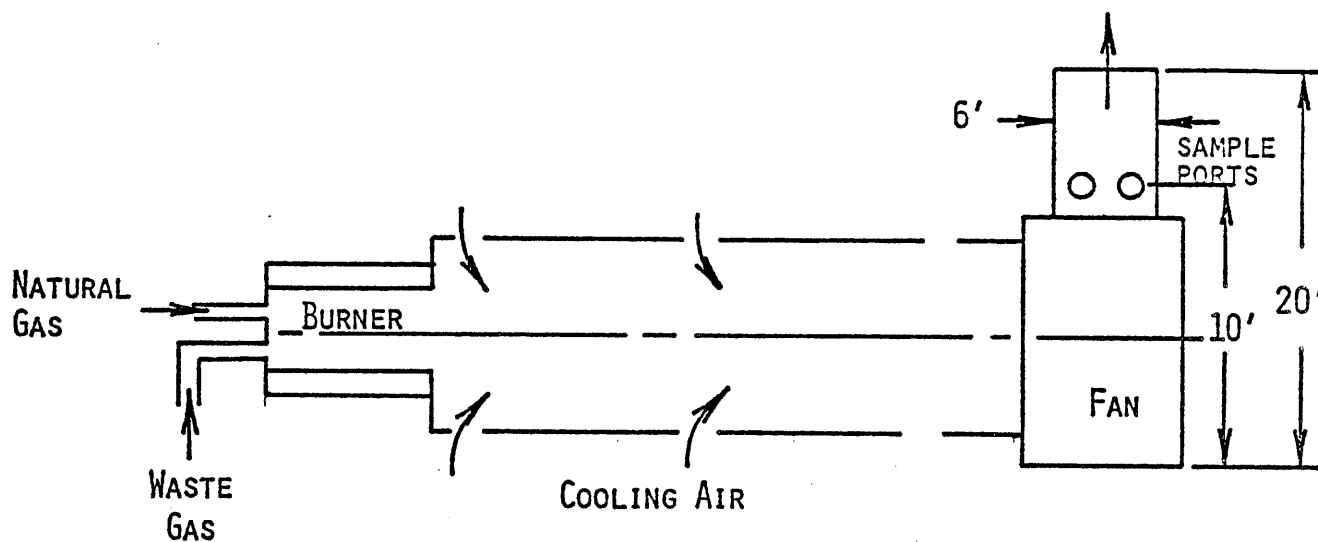
One refinery was found to have an odor abatement incinerator. This device is essentially a furnace fed by many pipes collecting waste gases from various refinery operations. As no previous source test data was available and sulfur content of the gas was unknown, a stack test was conducted. Test results (Appendix D) indicated that SOx concentration was 245 ppm, well below regulation levels and SOx emission rate was 40 lb/hr, or 0.5 tons/day. Since the device exceeded 2 lb/hr it was retained in the inventory, but no reduction potential estimate was made. The refinery operating this device reports that steps are currently in process to reduce emissions by 70% as part of an overall SOx reduction program and forecast emissions beyond 1974 are taken at 0.15 tons/day. No other refineries apparently operate this kind of device as all process off gas is treated by the amine systems.

An oil production field in Orange County operates an underground burning system to increase oil production. Exhaust gas from this process contains up to 4000 to 5000 ppm of H_2S (300 gr/100 CF). Nine vapor phase reactors (burners) were installed to replace iron oxide scrubbers and were apparently more effective in eliminating objectionable odors. One of the reactors has been removed and typically five to seven are operated to meet demand. Natural gas is fired in a refractory-lined combustion chamber to burn the waste gas for conversion of H_2S and other sulfur compounds to SO_2 . About 14 MMSCF per day of waste gas is burned. Burned products exit from the combustion chambers into large cylindrical mixing chambers where air is added for cooling prior to entry into an induced draft fan. The fan exit is upward through a short 20 foot stack on each burner system. Tests were conducted through existing 90 deg sample ports just above the fan. Table G-VI shows the reactor configuration and test sample ports. Test results obtained are also tabulated on this figure. Operation of these devices is continuous with five to seven of the eight units typically in operation at essentially identical flow conditions for all (verified by check of flow meters). Each unit then emits about 0.9 tons of SO_x /day with no seasonal variations. Total inventoried facility emissions with six units operating are 5.4 tons per day of SO_x with 0.15 tons of SO_3 emitted per day. Use of 0.5% S oil would result in 16 tons/day.

Potential reduction methods include flue gas scrubbing of the reactor exhaust or complete replacement of the reactors with a sulfur recovery system. Stack gas flow per unit is about 80,000 ACFM and scrubbers are estimated to cost about \$500,000 per unit or a total annual cost of \$975,000 per year for the six active units. At a 90% SO_x removal the cost effectiveness would be \$550 per ton of SO_x removed. Gas concentration and Claus plant costs at 14 MMCF/d are estimated to be about $\$1.75 \times 10^6$ (Ref. 87) with an annual cost of \$570,000, not including any savings from fuel not required. At 90% Claus plant efficiency the cost/benefit ratio would be \$312 per ton removed. The practicality of a Claus plant for 2-3 long tons of sulfur per day is not clear as the smallest known unit is rated at 9 tons/day.

TABLE G-VI

TEST SCHEMATIC AND RESULTS
FOR OIL FIELD VAPOR PHASE REACTOR



Test No.	Reactor No.	Stack Flow SCFM(wet)	% O ₂	SO ₂ ppm	SO ₂ lb/h	SO ₃ ppm	SO ₃ lb/h	SO ₃ /SO _x % vol
23-7	7	43466	19.5	163	71.6	3.0	1.7	1.8
23-6	6	43442	19.4	175	76.9	3.0	1.7	1.7

All data on wet basis

Moisture content, #7 = 4.5%, #6 = 5.1% H₂O by vol

G-4.0 COMMERCIAL, INSTITUTIONAL, AND INDUSTRIAL BOILERS

This class of devices includes all boilers with a firing rate of 10 MMB/h or more except utilities, those in refineries, and those in steel mills burning coke oven gas or blast furnace gas. Boilers are used to provide steam for industrial processes or for heating and to drive air conditioning turbines for commercial/institutional facilities.

Fuel usage rates are not as readily available for these boilers as in the case of utilities and refineries. The data accumulation was accumulation was accomplished during the NO_x study (Ref. 1) and no attempt was made to update the list or to revise capacity factor and fuel use patterns from the 72/73 data period. This introduces some uncertainty in the annual emissions for 1974 as more oil was undoubtedly burned. Also the assumption was retained that the boilers operate entirely on gas (if they can burn gas) in the summer and entirely on oil in the winter (if they can burn oil). Therefore the inventoried summer and winter values represent the lower and upper bounds of SO_x emissions possible from these boilers.

Sulfur contents for distillate fuels vary between 0.005 and 0.5% S, and residual fuels are close to 0.4% S. Actual 1974 values were taken where available. About 1% of the inventoried 1974 oil use was counted at 0.25% sulfur, an average based on typical distillate oils.

Most boilers in this category use light oils such as #2 distillate as the standby fuel during gas curtailment. Presumably, higher viscosity residual oils are not used because of the handling problems associated with oils that must be heated in order to be pumped and atomized. Since oil supplied only about 4% to 7% of the total annual heat input for most of these boilers during 1972-74, it is apparently more cost effective to burn the most expensive light oils than to install the necessary additional fuel systems to handle the less expensive heavy oils.

There are about 525 of these boilers in the boiler inventory, ranging in size from 10 MMB/h to about 200 MMB/h. Of these, all but about ten are rated at 100 MMB/h or less. About 20% burn only gas, about 70% burn gas with distillate oil standby, and about 10% burn gas with residual oil standby. In most industrial applications, these devices are characterized by high use factors. They tend to run 24 hours a day at a high percentage of maximum design load (approximately 80% to 110%). However, there is typically a 20% to 50% excess boiler capacity to allow full production with some of the boilers out of service. This means that each boiler is on line 70% to 80% of the year and down or on hot standby the remainder of the time. In most commercial/institutional applications, boilers tend to run full time also, but at lower loads (approximately 20% to 50%). Generally there is a 50% to 100% excess boiler capacity at these facilities with the result that each boiler is on line 50% to 70% of the year. In both cases, steam is typically generated all year, with relatively minor seasonal load variations.

A breakdown by fuel type of the boilers is given in Table G-VII, also showing SO_x emissions for each group. Total fuel use and emissions projections are shown in Table G-VIII. Projected emissions are 10 tons/day in 1980 with new gas supplies available and are 41 tons/day with no new gas supply. Distillate and residual oils are assumed as shown on the table. Approximately 15% of the oil use is residual. Having no specific data on future growth, the projections were based on the forecast of percentage growth of energy requirements for interruptible industrial customers of the Southern California Gas Company as submitted to the Public Utilities Commission (Ref. 40). The level of emissions in 1980 varies by a factor of 2 dependent on the amount of gas curtailment. A further switch to all residual oil at 0.5% sulfur would result in about 40 tons/day of SO_x.

SO₃ emissions from these boilers is currently only 0.03 tons/day but would increase to 0.9 tons/day in 1980 at projected fuel use levels.

TABLE G-VII

SOx EMISSIONS OF BOILERS BY FUEL TYPE

Type	Fuels	* Number	Size Range MMB/h	SOx Emissions Tons as SO ₂ /day		
				Aug	Dec	Annual
C/I	Gas	35	10-73	0	0	0
C/I	Gas and distillate	189	10-147	0	6.88	0.33
C/I	Gas and residual oil	22	10-50	0	1.18	0.05
Ind.	Gas	61	10-194	0.01	0.13	0.01
Ind.	Gas and distillate	189	10-186	0	9.65	0.35
Ind.	Gas and residual oil	<u>29</u>	10-66	<u>0</u>	<u>2.37</u>	<u>0.17</u>
		525		0.01	20.21	0.91

* 7 steel plant boilers not included, see Appendix L.

78 refinery boilers not included, see Appendix G-3.

TABLE G-VIII

FUEL USE AND SOx EMISSIONS PROJECTIONS
FOR COMMERCIAL/INSTITUTIONAL AND INDUSTRIAL BOILERS

Year	Gas (MMcf/y)	Alternate Fuel (equiv. MMCF)	Annual SOx Tons as SO ₂ /day
1974	48,471	2,425	0.91
1975	40,053	9,696	3.5
1976	31,967	21,472	8.8
1977	26,274	27,671	11.0
1978	13,022	41,433	16.5
1979*	12,318	43,156	17.2
1979**	0	55,474	39.4
1980*	29,658	26,324	10.4
1980**	0	55,982	40.0

*New gas supplies,
Dist. oil 0.25% S
Resid. oil 0.4% S

**No new gas supplies,
Oil at 0.5% S

5802-432

With current 85% distillate fuel use, reduction of sulfur content of distillate from 0.25 to 0.1% S, and residual from 0.4 to 0.2% S would result in a reduction of about 6 tons/day for the new gas supply condition. Should increased use of higher sulfur oil occur so that average sulfur contents increase to 0.5% S (within the current regulations) restriction of the sulfur content to the 0.2% S level would result in an additional fuel cost of about \$0.60 per barrel. This would result in a cost/benefit ratio of about 600 \$/ton of SO_x and would result in a prevention of a potential 25 tons/day of emissions in 1980. It should be pointed out that most boilers currently use distillate because of the more difficult and expensive handling procedures for residual oil and it is unlikely that many would convert to residual fuel even if it were cheaper than distillate. As with all combustion sources, limitation of gas curtailment through increase in Basin supplies is obviously the most cost-effective approach.

G-5.0 DOMESTIC AND SMALL COMMERCIAL/INDUSTRIAL SOURCES

Total natural gas use for these sources was estimated in Ref. 1 to be 379,340 MMcf/y in 72/73 and projected to increase to 448,100 MMcf/y in 1980. For average Basin natural gas content of 0.31 grains H_2S /100 CF, the total SOx emissions are only 158 and 187 tons SOx/y for 72/73 and 1980, respectively, corresponding to about 0.5 tons/day on an average, or about 2 tons/day if all gas use were concentrated in the three winter months. It is unlikely that any of these firm gas users would convert to oil and so there is no requirement for reduction potential estimates.

One small industrial source was tested in this program. A number of brake shoe relining companies operate gas-fired furnaces for brake shoe debonding to remove worn linings. Data entered in the EPA NEDS emission system (Ref. 22) indicated 12 tons SOx/year or a rate of 2.74 lb/h. LA APCD emission inventory data files indicated 44 tons/yr or 10 lb/h from this same facility. A brief survey of brake lining companies indicated at least nine other such devices are operated in the Basin. As the only possible source of SOx was the natural gas fuel and possible oil soaked in the lining material, it seemed inappropriate to inventory these devices at the 12 to 44 ton/yr level without further investigation.

As indicated in Table G-IX, the tests revealed that SOx emissions were only 0.2 lb/h or 0.0024 tons/day. As this result is under the inventory cutoff point of 2 lb/h, further consideration was terminated and the device was deleted from the inventory data base. It is believed that the higher levels of emissions in previous inventories were the result either of typographical tabulation errors or application of inappropriate emission factors.

TABLE IX

MEASUREMENT OF SOX EMISSIONS
FROM A BRAKE SHOE DEBONDING FURNACE

Test No.	Process Rate	Stack Flow SCFM (Wet)	Flue Gas Oxygen %	Flue Gas Moisture %	SO ₂ ppm (Wet)	SO ₃ ppm (Wet)	Emission Rates		SO ₃ /SOx % Vol
							SO ₂ lb/h	SO ₃ lb/h	
14	617 shoes/h	755	16.0	4.4*	27.	0	0.2	0	0

5802-432

* Estimated for natural gas fuel operation

G-6.0 STATIONARY INTERNAL COMBUSTION ENGINES

This category includes reciprocating internal combustion engines and industrial gas turbines. Reciprocating engines operate on firm natural gas supply and therefore are negligible sources of SOx. As shown in the inventory tables of Section 6.0, all emissions are less than 0.01 tons/day. Total gas use from the inventoried engines (98 groups of 488) was 7,353 MMcf/y resulting in only 3 tons of SOx/year. Conversion of these engines to operate on oil would be very costly. However, if done and 0.5% S oil were burned, the emissions would be about 5 tons/day.

Industrial gas turbines include primarily emergency standby units operated by the telephone companies. Nineteen of the engines were inventoried and about 246,000 gallons of distillate oil were burned in 72/73 with annual SOx emissions of only about 0.9 tons/year. Total gas use was 296 MMcf/y and if replaced with distillate oil at 0.25-0.5% S would result in an increase to only 0.1 to 0.2 tons/day.

Stationary internal combustion sources therefore are negligible sources of SOx and require no control attention. This is in sharp contrast to NOx emissions with NOx reductions achievable in reciprocating engines being identified as one of the most cost-effective NOx control approaches (Ref. 1).

G-7.0 CONCLUSIONS

Utility boilers are currently the dominant source of oxides of sulfur with the 70 basin units emitting 172 tons/day on an annual basis in 1974. This year was unusually low as large amounts of hydroelectric power were imported. If this power had not been available it is not clear whether the added power would have been provided by oil or gas but it probably would have been oil. Return to normal generation rates and additional growth plus virtually complete gas curtailment, indicate that by 1980 the utilities will emit 404-459 tons/day of SO_x and of this 15 tons/day as SO₃ will be emitted. The most cost effective control is to rapidly restore the natural gas supply. However, failing this, should it be determined necessary to limit the SO_x increase, the most cost effective method for obtaining reductions relative to a 0.5% S equivalent level would be to further desulfurize the fuel to a level between 0.5 and 0.2% S as required to meet air quality standards. The cost/benefit ratio of this approach is estimated to be \$300-600/ton of SO_x for a reduction of up to 220 tons/day at between 0.2 and 0.5% sulfur. Any additional costs required to desulfurize higher sulfur fuel have not been counted as regulations currently require that level.

Scrubbers were evaluated and found to have a cost/benefit ratio averaging about \$400-1350/ton reduced. In compiling these costs, as with desulfurization the reduction is considered only from the 0.5% sulfur level equivalent.

Other combustion sources include industrial, commercial and institutional boilers. There are about 525 of these units in various industries, and institutions. Of these 429 currently burn oil at 0.2-0.5% sulfur. The units emitted 1 ton/day in 1974 and are projected to emit 10-41 tons/day in 1980. Restriction of fuel sulfur to 0.2% would result in a reduction of 25 tons/day in 1980 at a cost/benefit ratio of

\$600/ton of SO_x reduced. The costs were based on actual estimated desulfurization costs and therefore may not necessarily reflect actual purchase costs. However as more low sulfur oil is used the purchase costs are expected to more nearly reflect manufacturing cost as is now the case for gasoline (Appendix F).

Fuel burning in the petroleum industry resulted in SO_x emissions of about 11 tons/day in 1974. With new gas supplies this is estimated to grow to about 25 tons/day by 1980. However, with no new gas supplies, up to 50 tons/day could be emitted. Restriction of fuel oil sulfur content would reduce these emissions by about 28 tons/day at a cost/benefit ratio of \$600/ton at a 0.2% S limit.

Other combustion sources considered include eight vapor phase reactors that burn oil field waste gas and unit 5.4 tons/day in Orange County. Should reductions of this source be necessary, the most cost effective approach would appear to be installation of a gas concentration plant (amine scrubbing) and a Claus sulfur recovery plant. The cost/benefit ratio of this would be \$312/ton reduced and the reduction would be 5 tons/day. Claus plants of the small size required for this source may not be practical. The use of scrubbers would achieve a similar reduction but at a higher cost/benefit ratio of \$550/ton.

Domestic, small commercial/industrial sources and internal combustion engines were considered, but for the most part burn firm gas or only small quantities of oil. The emissions are negligible and no consideration of reduction potential was necessary.

REFERENCES

1. Bartz, D. R., et al. "Control of Oxides of Nitrogen from Stationary Sources in the South Coast Air Basin of California," KVB Engineering, ARB-R-2-1471-74-31, PB-237688/7WP, Sept. 1974.
12. Los Angeles County Refinery Fuel Use and Emissions for August 1972-December, 1974, LAC APCD.
13. Cantrell, A., "Annual Refining Survey," Oil and Gas Journal, Vol. 73, No. 14, pp. 96, April 7, 1975.
22. "Point Source Emission Inventory for Los Angeles County" EPA, Basic Ordering Agreement 68-02-1004, Task 2; Pacific Environmental Services, R. W. Bryan, February 1974.
40. "1975 California Gas Report," Prepared Pursuant to California Public Utilities Commission Decision 62260, Sept. 1, 1974.
76. Cato, G. A., et al., "Field Testing: Application of Combustion Modifications to Control Pollutant Emissions from Industrial Boilers - Phase I," EPA-650/2-74-078a, October 1974.
77. Wilson, A. J., "Measurements of Emissions from Steam Generators at Two Power Plants in Los Angeles County," Los Angeles Air Pollution Control District, Technical Report for California Air Resources Board Contract 4-286, 1974.
78. Private Communication from Southern California Edison Company, August 20, 1973, October 26, 1973, June 18, 1974, July 5, 1974, July 31, 1974, September 12, 1974.
79. Private Communication from Los Angeles City Department of Water and Power, August 20, 1973, September 19, 1973, June 24, 1974, and August 16, 1974.
80. Private Communication from Glendale Public Service, August 20, 1973, October 31, 1973, May 8, 1974.
81. Private Communication from Burbank Public Service, August 20, 1973, August 31, 1973, July 10, 1974.
82. Private Communication from Pasadena Department of Water and Power, August 20, 1973, October 8, 1973, June 12, 1974, June 27, 1974.
83. McGlamery, G. G., et al., "Detailed Cost Estimates for Advanced Effluent Desulfurization Processes," TVA, EPA 600/2-75-006, Jan. 1975.

84. Koehler, G. and J. A. Burns, "The Magnesia Scrubbing Process as Applied to an Oil-Fired Power Plant," EPA 600/2-75-057, PB 247201, October 1975.
85. Wet Scrubber Newsletter, The McIlvaine Comp., Number 21, March 31, 1976.
86. State of California, Air Resources Board, Staff Report on "The Feasibility of Reducing Sulfur Dioxide Emissions from the Burning of Fuel Oil," Report 76-2-3, January 16, 1976.
87. Nelson, W. L., "A Look at Sulfur-Recovery Costs," Oil and Gas Journal, pp. 120, March 18, 1974.